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Proceedings of the eleventh cotton utilization research conference

held at New Orleans, La.,
May 10-12, 1971

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PREFACE

The Cotton Utilization Research Conference is sponsored annually by USDA's Southern Marketing and Nutrition Research Division to report progress made in cotton research. Topics discussed at this year's meeting covered a wide range of vital interest in expanding the use of cotton, including mechanical processing, blends, flame resistance, soil resistance, and durable press in woven and knitted fabrics.

These proceedings report in summary the statements presented by the various speakers during the conference.

C. H. FISHER, Director
Southern Marketing and Nutrition Research Division

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WELCOME

by

C. H. Fisher, Director
Southern Marketing and Nutrition Research Division
New Orleans, La.

We thank Mayor Moon Landrieu of New Orleans for sending his special aide to our conference to convey his message of welcome, and for the special tribute to Dr. Benerito for her research accomplishments. We at the Southern Marketing and Nutrition Research Division (SMNRD) also are proud of Dr. Benerito – Ruth to us – and extend our own congratulations.

We are honored to have so many busy and important people come from far away places, even from other countries, to participate in this meeting.

It is good to be able to say that the situation for cotton is better this year than it was at the time of last year's conference and that cotton producers are justified in taking a more cheerful view of the future. No doubt our honorary chairman, Charles R. "Jerry" Sayre, will have more to say about this.

Among several reasons for this more cheerful outlook is the expanded program of Cotton Incorporated; probably our general chairman, J. Dukes Wooters, will mention this.

As you probably know, the principal purpose of this annual Cotton Utilization Research Conference is to provide an opportunity for us to report promptly the advances we have made during the past year in our cotton research, and for us to obtain your opinions and comments on our research program and the work we are doing. We invite the free expression of your views, even if these views may be critical on occasion. We hope that the interchange of information will not be limited to these conferences. We invite you to visit us or communicate with us at any time during the year.

Information about our research results is disseminated in a number of other ways. These results are published in approximately 150 papers each year on cotton. USDA's Extension Service and the Information Division of the Agricultural Research Service provide valuable assistance in making known our research findings. Two representatives of the Extension Service who are particularly helpful are Larry Heffner, stationed at Raleigh, N.C., and Bill Martin, stationed at Clemson. The ARS Information Division, headquartered in Washington, D.C., is represented in New Orleans by Vernon Bourdette, who publicizes our research through press releases, articles, and by means of exhibits, radio, and television.

You may remember that we have a Textiles and Clothing Laboratory, located on the campus of the University of Knoxville, in Tennessee, where the staff works closely with the Home Economics Department.

We are pleased to announce that a distinguished textile scientist, Mary E. Carter, has joined our organization as Chief of this Textiles and Clothing Laboratory. Many of you know Dr. Carter or know of her notable career in textile research. A native of Georgia, Dr. Carter received her Ph.D. in Chemistry at the University of Edinburg, Scotland, and has worked at Calloway Mills and American Viscose. She recently published a book on the chemistry of textile fibers. We are proud to have Dr. Carter as the head of the Textiles and Clothing Laboratory.

Although we announced last year that there has been a change in the patent policy of the Department of Agriculture, I would like to call your attention to the fact that the Department can now grant exclusive licenses under some patents in certain circumstances. This new flexibility may interest some of you.

I hope that this conference will be highly successful and helpful to everyone attending. I cordially invite you to visit our Laboratory while you are in New Orleans and at any other time you may wish to do so.

FUTURE OF COTTON

by

Charles R. Sayre
Staple Cotton Cooperative Association
Greenwood, Miss.

I am honored and happy to meet with you today to discuss the Future of Cotton. That is not a statement I could have made so easily during the decade through which we have just passed – the dismal 1960's.

Let's recall briefly some of the changes which took place in our industry during the 1960's.

Synthetic fibers – mainly the polyesters – cut deeply into cotton's apparel, household, and industrial markets in this country. Consumption of U.S. cotton at home amounted to 9.0 million bales in 1959–60, but had dropped to 8.0 million in the 1969–70 marketing year. Much of this cutback in our markets was from imported yarns, cloth, and garments. Last year's textile imports were 2.6 million cotton bale equivalents – almost three times the 1960 level.

Exports were 7.2 million bales in 1959–60, an unusual year to be sure, but were down to 2.8 million bales in 1969–70.

The number of cotton farm allotments, gins, and mills has decreased substantially. Allotments dropped from 951,000 in 1960–61 to 514,000 in 1970–71; cotton gins declined from 5,395 in 1960–61 to 3,754 in 1970–71; textile mill plants, on the basis of recent data available from census, show a decrease to 845 from the previous figure of 939.

This has reduced job numbers, and out-migration of workers has continued at a rapid rate from several major cotton-producing States.

Capital requirements have increased and now average in the neighborhood of $125,000 per worker on a modern and efficient cotton operation compared with about $41,000 per worker in industry.

This picture of the 1960's was pretty discouraging to cotton farmers, and to all other segments of the cotton industry. It took a lot of courage to talk about the future of cotton in the past decade. It took a lot of courage even to think about cotton's future. But my hat is off to all of those people in Government, in industry, and in the organizations of the cotton industry who continued to think about cotton, to work with cotton, and to plan for the future. Those people have kept cotton in business in the face of the worst odds ever to face a major commodity. Now there are signs that we have indeed turned the corner and that better times lie ahead.

Last year cotton increased its share of all fibers moving through the cotton spinning system for the first time in 10 years, and this in a period of textile recession.

Exports in 1970–71 are estimated at 3.5 million bales. This is still much too low, but moving upward. Our historical share of the world market is more than 5 million bales annually, and exports of this level at a minimum are essential to maintain farm income, a favorable trade balance, and to underpin dollar values.

The Agricultural. Act of 1970, a 3-year law, has reduced uncertainties for most farmers. It allows production to move into the hands of those who want to grow cotton; it provides a greater incentive to do a better job of growing and harvesting; and it at least doubles the research and promotion programs of Cotton Incorporated. We are working hard to have 30 million plus dollars available to CI in 1972 and 1973. This will provide the largest and most effective commodity program of any group.

Favorable market pickups have occurred in corduroys and denims, fabrics for printing, and more recently, in cotton knits. On the production side, the narrow-row, high-plant-population cotton culture, with 100 percent chemical weed control and once-over harvesting, raises exciting possibilities for sharp reductions in the cost of growing cotton.

These and other developments make it possible to talk about the future of cotton with confidence. The topic is especially appropriate for this meeting here today, because here are gathered the allies and partners in a teamwork approach which has accounted for so much of the progress we have made.

This cotton team includes the Government agencies, and particularly our hosts from the USDA cotton utilization and development group, and their colleagues in production and marketing research and in Extension.

The team includes the industry firms, many of whom are represented here today in the audience or on the program. This includes textile mills, finishers, and the chemical industry.

And the team includes the organizations of the raw cotton industry: The National Cotton Council, which I have the honor of serving this year as president, and Cotton Incorporated, about which you will hear from its executive vice president and general manager, Dukes Wooters.

The favorable stage we have reached is largely due to the combination of efforts by this joint Government-industry-cotton organization team. It seems to be providing a turnaround for cotton. We have some momentum now, and I think we can build on it and generate new confidence in the future of cotton.

This is no time for complacence, however. It is not the time to let down, to rest on our oars. As a matter of fact, now, when we have the opportunity to exploit some new possibilities, it is more important than ever that the various members of cotton's team fit their efforts together more neatly and more tightly for maximum effectiveness.

I want to say just a few words about the members of this cotton team, in part to recognize their contributions, and in part to point out how each of these agencies and organizations can complement and support the work of the others as we move ahead.

First, let's recognize our friends in Government, mainly the USDA and State Experiment Stations. Here is where the bulk of cotton's research effort has been and is still being carried out. We are highly dependent on this effort; we recognize the major contributions it has made over the years; and we will do our best to help build these programs still further to help meet the great challenges of the 70's.

I am grateful to have this opportunity to express the deep and sincere appreciation of the raw cotton industry for the many important contributions of the Southern Regional Research Laboratory here in New Orleans. I won't attempt to enumerate them all, but will cite just a few examples.

This laboratory – the SRRL – has pioneered the development of fire-resistant finishes for cotton, and in so doing has become the leading research organization on flame-resistant finishes in the world. Largely as a result of this work, the cotton industry can adapt to the new standards under the Flammable Fabrics Act, and cotton products can provide greater fire safety for the general public.

This laboratory has carried out, reported, and published much basic work on the functioning of durable press finishes in cotton. This has helped industry to move ahead with better finishes for cotton and cotton-blend fabrics.

Basic work on cotton-fiber structure and on the processing parameters of various qualities and staples of cotton has helped mills to increase the efficiency of their processing.

New machinery for cotton, such as the SRRL opener-cleaner, improved high speed carding, and other developments, got their start here at the New Orleans laboratory.

I could go on with the list, but the point I wish to make is that these contributions are recognized by our industry; they are deeply appreciated; they have both helped and encouraged the cotton industry. We are counting on the SRRL to continue playing a major role in the overall cotton research effort, along with other divisions of USDA. We pledge our full support in maintaining and building your programs further.

I also want to acknowledge the part which textile mills, finishers, and the chemical industry have played in bringing us to the more encouraging position we find ourselves in today. No new product of research will sell a single bale of cotton until it is adapted and put into production. The continued interest which industry has had in cotton – as evidenced by the fine industry turnout today – has been one of cotton's main sources of strength.

As we look to the future, obviously the decisions made in Washington will affect us vitally. We must stimulate critically needed investments in cotton's research and extension programs. We have a continuing battle on payment limitations. The crucial problem on textile import restraints is intensifying.

Another member of cotton's team – the National Cotton Council – has demonstrated its effectivness in Washington time and time again – most recently and impressively in the uphill fight for a new cotton program.

It has bolstered the cotton research and extension program of the land-grant universities and the U.S. Department of Agriculture.

It is involved in a continuing effort to make sure that legislation or Government regulations, or both, do not work against cotton in the vital area of textile flammability, or pesticides, or pollution, or a host of other subjects involving technology.

But the Council also carries out major programs of public relations, of economic and marketing research, of foreign-market development, and of stimulating industry interest and efforts on cotton.

The Council is an organization which tries to get the overall job done for cotton – whether it's through the industry, the Government, or private firms allied with cotton.

The newest member of the cotton team is Cotton Incorporated. You will hear about the programs of Cotton Incorporated from its executive vice president, Dukes Wooters. I have known Dukes as long as, or perhaps longer than, anyone in the cotton industry. He is talented, even-handed, and in a hurry. You'll enjoy working with him. You can tell from what he says about the grower-supported research and promotion program that Cotton Incorporated doesn't replace any other program; it doesn't substitute for any other research; it doesn't do what Government, or industry, or the Cotton Council do in their respective fields.

But Cotton Incorporated is a great new program for the cotton industry, a dynamic new force, it will bring out the "new" in cotton and sell it. CI is another reason to be encouraged about the future of cotton.

Where is that future – the Future of Cotton?

The next 3 years to 5 years will be of great consequence to cotton. Hopefully, textile markets will not experience the surges of new and unmatchable fibers. Projected increases in manmade fiber production capacities have been pared. Their expansion will be at a reduced rate. Emphasis upon nature and the environment will spotlight and add prestige to natural fibers. Attention to the plight of the "have nots" around the world will increasingly go beyond nutrition into the reaches of comfort and the aesthetic.

Those interested in a stable future for cotton with a growth dimension in it must use this pivotal period to the greatest possible advantage.

What prospective advances are apparent that can become real in 3 to 5 years – to cotton's benefit?

1. Although cotton has been playing catchup, knitting may give it a lift.

2. Durable press – new processes and a superior bundle of properties may be close with "high cotton" blends.
3. Cotton now has its biggest war chest ever for research, product development, and promotion – the largest of any farm group.
4. Cotton offers a team approach from cytogenetics to the consumer. It's up to each of us, all of us, continuously to help capture the vigor of a team approach and to build added momentum with it.
5. Now is the time to "crash in" with early payoff results from cumulative findings. I feast upon such statements in the program of this meeting:

   (a) "cotton fabric abraison resistance is increased 50 percent"
   (b) "preliminary results indicate that further development should soon make this mercerizer available to the textile industry"
   (c) "all the experimental fabrics are considered marketable without discounted penalties"

Granted I have taken these statements out of context, but they reflect early payoff potentials.

6. The cotton industry increasingly is structured to embrace the "new" with less delays.

May I quote a good friend, Bud Greer, immediate past president, Georgia Textile Manufacturers Association, from his address at their convention last month.

> "Short and frequent production runs will be successful alternative to the long, steady, continuous runs with which we have been accustomed. Textile mills must have the short production run and frequent change capabilities to satisfy the immediate and ever changing consumer demand."

He's right and this will help cotton.

On the production and handling side there are important developments.

1. Simplified approaches to close-spaced, full chemical weed control, and once over harvesting looks promising. (Parenthetically we may get a side benefit of greater fiber uniformity with only a few bolls on individual plants).
2. A new phase of boll weevil research – pilot area eradication – is underway. It should work.
3. Effective translocatable herbicides for deep rooted perennials are closer at hand.
4. Lash and containerized export shipment – interior to interior – are working with substantial savings.
5. Net weight trading, standard compression at the gin, and added moves for new packaging are signs of a traditional industry on the move.

With the current turnaround in consumption and exports, the intermediate future can be made favorable if the coordinate team efforts jell – government, industry and cotton organization. I think they will.

We have reason for optimism. With full efforts we can go forward and indeed make a future for cotton in the United States.

SESSION I: Burton Blagman, Phillips-Van Heusen Research & Development Corp., Waldwick, N.J., Chairman

INFRARED SPECTRA OF EXTRACTS OF SELECTED FLAME RETARDANT AND FLUOROCHEMICAL FINISHED COTTONS

[SUMMARY]

by

Nancy M. Morris and Elizabeth R. McCall
Southern Marketing and Nutrition Research Division
New Orleans, La.

(Presented by Nancy M. Morris)

For several years there has been considerable interest in developing methods of identifying additives present in finished fabrics. Acid hydrolysis of the fabric followed by infrared spectroscopic examination of the hydrolyzate has proved to be a reliable method[1] for identifying many of the crosslinking reagents in use today. However, the situation for other additives is quite different. At present, an extraction procedure is being developed to successively remove various additives from the fabric undergoing analysis. Extraction is followed by subsequent spectral identification of the finish present in each fraction. In this study, fluorochemical and flame-retardant finishes are added to the functional categories previously examined.

Several fluorochemical finishes were examined with successive extractions of hexane, trichloroethylene (TCE), methanol, water, and hydrochloric acid. The hexane extracts of all of these fabrics contained small to moderate amounts of the fluorochemical, depending on whether or not a polyethylene softener or lubricant was used in the preparation of the fabric. In those instances where polyethylene was used along with the fluorochemical, very little of the fluorochemical was extracted by the hexane. TCE extraction yielded large amounts of a material, the infrared spectrum of which very closely matched that of the fluorochemical as received. It was not possible to use the infrared spectra to distinguish one fluorochemical from another because of the similarity of the spectra of these reagents. Even on an as received basis the spectra were far too similar to allow reliable identification of the specific fluorochemical. However, identification of the finish as a fluorochemical type is very reliable. The methanol, water, and HCl extracts of fabrics treated with fluorochemical alone produced no useful infrared spectra. The methanol and water extracts of fabrics treated with fluorochemical in combination with a crosslinking reagent contained apparently unreacted crosslinking reagent, and the HCl extract produced a spectrum which in each case matched the hydrolyzate spectrum of the crosslinking reagent used to treat the fabric. It is concluded that, although it is relatively easy to identify a fluorochemical finish as such, it is not possible to distinguish the specific fluorochemical used and that the presence of a fluorochemical finish does not interfere with identification of the specific crosslinking reagent used.

A number of flame-retardant fabrics were examined, including specimens with a commercial (Pyrovatex) finish and others based on processes developed at SMNRD. The hexane extracts of the Pyrovatex fabric produced a very weak spectrum. TCE extracted a mixture of polyethylene (or polypropylene) and the Pyrovatex reagent. It is not known why the polyethylene did not come off with hexane. The methanol and water extracts both contained Pyrovatex, and it is definitely possible to identify this treatment from these two extracts. The acid hydrolyzate spectrum of the Pyrovatex-treated fabric is identical with the hydrolyzate spectrum of the Pyrovatex reagent. Thus, identification of a specific crosslinking reagent, if one were used in combination with this flame retardant, would be difficult.

A THPOH-amide-treated flame-retardant fabric was also evaluated by successive solvent extractions. Again, the hexane and TCE extracts indicated that these fabrics had been treated with polyethylene.

Spectra of the methanol and aqueous extracts of the fabrics treated with THPOH-amide are reproducible. They are not, however, identical with each other or with the spectrum of the reagent itself. It would be possible to identify this finish from the extract spectra by comparison with extract spectra from a known finished fabric. The spectra of the acid hydrolyzates of these fabrics do not resemble the hydrolyzate spectrum of the reagent itself. Again it is necessary to compare these spectra with those of hydrolyzates of fabrics of known composition. In this case the acid hydrolyzate spectrum did not provide additional information. The hydrolyzate spectrum should, however, be checked for the presence of other additives, even though specific identification of these additives may not always be possible in the resulting mixture.

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[1] Miles, S. H., McCall, E. R., Tripp, V. W., and O'Connor, R. T. Infrared spectra of hydrolysis products of cottons reacted with typical nitrogenous crosslinking agents. Amer. Dyestuff Rptr. 53: 440-444. 1964.

The results obtained by the successive solvent method of extraction was compared with the results obtained in a previous study[2] in which the TCE extract was separated into component fractions using a chromatographic column. It was found that the column separation was superior to the successive solvent extraction method. However, use of the column is so time consuming that the successive solvent method is recommended for all fabrics. In those instances where no spectral match can be obtained by this technique, the column chromatographic technique should then be used.

It was also found in this study that the simple beaker method of extraction resulted in separation of components equal to that obtained by the more elaborate Soxhlet method. The beaker technique is much more rapid and is therefore superior for qualitative work.

Although much work remains to be done before a truly reliable method is available, the method thus far developed is useful in the identification of many additives. The major requirement for the successful identification of more finishing agents is an extensive catalog of reference spectra.

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[2] McCall, E. R., Morris, N. M., Tripp, V. W., and O'Connor, R. T. Identifying softeners and fabric additivies by infrared spectroscopy. Textile Chem. Colorists 2: 105-116. 1970.

CRYSTALLITE ORIENTATION IN CELLULOSE FROM SEVERAL VARIETIES OF COTTON
[SUMMARY]

by

Jacques J. Hebert, Charles R. Esposito, and Jarrell H. Carra
Southern Marketing and Nutrition Research Division
New Orleans, La.

(Presented by Jacques J. Hebert)

A cotton fiber is a flat, ribbonlike convoluted tube made up primarily of cellulose. This cellulose is in the form of thin fibrils that are arranged about the axis of the fiber in a helix. It is believed that almost 95 percent of the cellulose present within these fibrils is more or less crystalline in nature. Since many of the mechanical properties associated with cotton are dependent upon the crystallites within these fibrils, much attention has been applied to studies of their size, shape, and orientation. This report is concerned mostly with the orientation of these crystallites with respect to the axis of the fibrils after these fibrils have been removed from the fiber.

It has already been reported that the helix, or spiral angle, that the fibrils form with the fiber axis is approximately 22° and that this angle appears to be constant among all genetic varieties of cotton. To arrive at the distribution of crystallites about the fibrillar axis, electron diffraction studies were undertaken.

Samples of several varieties of cotton as well as ramie and chemically modified cotton were beaten in water in a laboratory blender until the fibers were fragmented into discrete bundles of fibrils. These fibril bundles were placed on electron microscope grids and dried under vacuum. The specimens were then placed in an electron microscope and their electron diffractron patterns recorded on glass photographic plates. The patterns obtained from the native cotton specimens were charactertistic of the generally accepted cellulose I lattice exhibiting a relatively high degree of orientation about the fibrillar axis.

Each fibril pattern was photometered azimuthally about the 002 reflection – the most intense reflection in a cellulose I diffraction pattern. This reflection originates from the plane that is proported to be parallel to the molecular chain axis; therefore, this orientation measure is implicitly indicative of molecular orientation. The resultant photometer tracings could be represented by an exponential curve of the type,

$$I=I_m \exp\left[\frac{-\ln 2}{(\alpha)^2}\right](\epsilon^2)$$

where α = angular width of the distribution at one-half the maximum intensity, and ϵ = the azimuthal scan angle. The values of α, or the crystallite orientation angles, for 10 varieties of cotton are given in table 1. It can be seen that there is little difference in alpha apparent among the varieties. Analysis of variance among angles for all specimens indicated no significant differences among variety samples.

Table 1. Crystallite orientation angle of 10 cotton varieties

Variety	α(°)	Standard error
Mysore American	9.5	0.46
Devity	10.4	.30
Bobshaw	10.7	.68
Laxmi	9.5	.33
Pima S-1	9.4	.07
Stoneville 2_B	9.4	.28
Gaorani 12	10.6	.85
Del Cerro	11.1	.64
G. Aboreum	9.8	.40
St. V. Sea Island	9.2	.70

As a standard for comparison, ramie, a highly oriented cellulose fiber, was studied. The angle of orientation for ramie was significantly lower than those for native cotton – the value for ramie being approximately 6°. The X-ray angle determined for a bundle of ramie fibers is essentially the same as this value, whereas the X-ray bundle angle for cotton fibers of these genetic varieties ranged from 25° to 38°. This illustrates the effect of such gross fiber factors as helix, or spiral angle, and convolution angle on X-ray bundle orientation measurements. Ramie has no appreciable helix or convolution angle and, therefore, the bundle value being undistorted approaches the value of fibrillar orientation.

In an attempt to understand the effect of mercerization on crystallite alinement, a sample of Deltapine cotton, an American Upland fiber, was treated with a four normal caustic solution until complete lattice conversion occurred. The values of alpha for the treated sample as well as the untreated control appear in table 2. As expected, the swelling in caustic tends to disorder the fibrils as evidenced by the increase in alpha for the treated sample. It might be pointed out that X-ray bundle angles of mercerized cotton usually show little or no change in orientation from untreated samples unless some tension is applied and then the angles decrease. The effect can be attributed to the change in convolution angle brought about by the tensioning which tends to distort the disorienting effect of caustic swelling on fibrils within the fiber. Inasmuch as the fragmentation technique would relax any strains induced by tensioning, no attempt was made to evaluate the effect of tensioning at this time.

Table 2. Crystallite orientation angle of mercerized cotton

Sample	$\alpha(^\circ)$	Standard error
Control	9.7	0.65
4N. NaOH	13.2	1.22

In conclusion, we can say that crystallite orientation in cellulose fibrils can be measured by electron diffraction techniques. Further, the crystallites in fibrils removed from cotton fibers are inclined to the fibril axis with an angle of approximately 10°. Variety or genetic species seems to have no effect on this orientation. The crystallites in ramie are more closely alined to the fibrillar axis than those in cotton, that is, alpha equals 6° in ramie and 10° in cotton. Also, swelling in caustic, to the extent that lattice conversion takes place, tends to disorient the crystallites in cotton fibrils. This is evidenced by an increase of 30 percent in the crystallite orientation angle, alpha.

POROSITY OF MODIFIED COTTONS BY GAS ADSORPTION [SUMMARY]

by

Blanche R. Porter and Eileen K. Boylston
Southern Marketing and Nutrition Research Division
New Orleans, La.

(Presented by Blanche R. Porter)

The physical adsorption of condensable vapors has been used to study the internal surface and structure of many different types of porous solids.[1] The application of this method to cotton lint fibers after various treatments was shown to reveal significant differences in the amount of internal surface available to nitrogen at liquid nitrogen temperature.[2] More detailed analyses of complete adsorption isotherms show that significant indications of changes in pore structure of cotton fibers are also revealed by adsorption studies. Experimental methods and instrumentation were described in the previous publication.

The size and shape of the hysteresis portion of an adsorption isotherm is a function of the detailed pore structure of the adsorbent and qualitative differences in structure may be evaluated by inspection of the comparative shapes of these regions for different samples. However, the procedures developed by Cranston and Inkley[3] were used to obtain analyses of pore size distributions from both the adsorption and desorption branches in the hysteresis region of the isotherm, from approximately 0.4 to 0.93 relative pressures. This analysis is based on a cylindrical pore model and uses the Kelvin equation, which relates pore diameter to relative pressure. The pore size distribution is obtained by plotting the rate of change in volume adsorbed as a function of pore diameter. Although many investigators consider the desorption branch of the isotherm to represent true equilibrium and state this branch should be used for pore size distribution, adsorbents such as cottons that have maximum volume in pores less than 37 to 42 Å in diameter are best compared with calculations from the adsorption branch. This conclusion is based on the presently well established finding that there is a minimal poor diameter, approximately 40 Å, below which all capillary adsorbed nitrogen will evaporate.[4] The method of Brunauer, Emmett, and Teller (BET)[1] was used to calculate surface areas from data at approximately 0.1 to 0.35 relative pressure.

The three treatments shown in table 1 caused maximum increases in surface area in all the samples studied. In the series of samples treated with increasing concentrations of phosphoric acid and undried before sample preparation, the height of the hysteresis curve increased with increasing concentration through the 81 percent concentration; at 85 percent concentration, the height decreased and the shape of the curve showed a significant change. Analyses of these portions of the isotherms showed a continuous broadening of the pore size distribution with increased concentration of phosphoric acid, as shown in table 1. Changes in crystallinity[5] were discernible only at a concentration of 85 percent acid; the Cellulose I structure was still shown but with significant diminution in peak heights. Electron micrographs[6] showed increasing lamellae separation and comminution of lamellae through the sample treated at 81 percent concentration. There was evidence of extensive fibrillar fusion and loss of lamellae structure after treatment at 85 percent concentration.

Maximum change in shape of the hysteresis portion of the isotherm among samples treated with 5.0 M sodium hydroxide was observed in the sample treated in a slack condition and exchanged to helium without intermediate drying. There was some broadening of the pore size distribution in all three samples, although in the air-dried, slack-mercerized sample this was not sufficient to shift the value of pore diameter at maximum peak height. X-ray data showed incomplete conversion to Cellulose II in each sample. A distinct change was found in fibrillar aggregation of the sample after mercerization, as shown by electron micrographs of the fibers undried before embedding with methacrylate; the lamellar structure of the native cotton had been replaced by a sponge-like texture. When embedded after drying there was evidence of decreased swelling of the cross section and some blurring of the spongy texture.

The sodium salt of phosphonomethylated cotton at a D.S. = 0.08 yielded a sample with an adsorption isotherm similar to that of the undried mercerized sample, although the phosphonomethylated samples were dried after treatment and reswollen for adsorption study. The isotherm of the more highly substituted sample resembled that of the sample treated with 85 percent

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Table 1. Treatments

Sample treatment	HET surface area (Percent control)	Pore diameter at maximum peak Ht. (Å) Adsorption	Desorption	Crystallinity 101/102 (dried samples)
Phosphoric acid, aqueous				
Percent concentration:				
75	201	27.5	37.5	0.22
77	456	27.5	42.5	.21
81	798	32.5 to 42.5	42.5	.20
85	479	32.5 to 52.5	42.5	.34
Sodium hydroxide 5.0 M, aqueous:				
Undried, slack	382	32.5 to 42.5	37.5 to 42.5	.35
Air dried, slack	172	27.5	37.5	.39
Air dried, tension	74	27.5 to 42.5	37.5	.32
Phosphonomethylated (sodium salt):				
DS = 0.08	327	37.5 to 52.5	42.5	1.44
DS = .14	103	37.5 to (very broad)	42.5 to 47.5	1.37
Control	100	27.5	37.5	

phosphoric acid. The significant increases in pore diameters at maximum peak heights are shown in table 1. It is apparent that this phosphonomethylation permits reswelling of the cotton to approximately the same extent observed in undried mercerized cotton, at the lower degree of substitution, as shown by the increase in surface area to 327 percent of the control sample. X-ray diffractograms showed significant decrystallization, but the cellulose II pattern was still present at a D.S. of 0.08; at the higher D.S., there was little indication of any peak formation.

A measure of surface area can be obtained from the analyses for pore size distributions and compared with the area calculated by the BET method with data from the lower part of the isotherm. Agreement of area values has been used by some to indicate different pore shapes. In our studies, BET areas for 50 samples were compared with areas determined from the analyses of the hysteresis portion of both the adsorption and desorption isotherms. Samples treated with 81 percent phosphoric acid, the undried mercerized sample, and the two phosphonomethylated samples showed maximum differences in these areas, over 20 percent, when areas were calculated from desorption isotherm data, compared with differences of less than 7 percent with areas from the adsorption branch, for all but the phosphonomethylated sample of D.S. = 0.08 (12 percent). This comparison has been interpreted to denote the formation of bottle-necked pores. Forty-five samples agreed, within 10 percent, with the adsorption branch and 39 with the desorption branch; and half the samples agreed in area within less than 5 percent with either branch. These findings would indicate a definite change in pore shape of the high area samples and of each phosphonomethylated sample.

In adsorption tests of other treated cottons, most changes in hysteresis were not significant. However, the surface areas of these samples varied widely. Surface area values (as percent of the control sample) of some of these cottons are shown below.

Zinc chloride – 140 percent
Potassium thiocyanate – 154 percent
Lithium chloride – 160 percent
(each 5.0 M, aqueous)
Boiling distilled water – 159 percent
Urea – 166 percent
Dimethylformamide – 121 percent
Dimethyl sulfoxide – 159 percent
(each 50 percent aqueous)

In most of the durable-press treated samples, surface areas were too low to permit accurate data for isotherms, except for a few samples. Surface areas were reduced to less than 43 percent of untreated samples in the following: CH_2O – Vapor Phase, Dry Cure, and Form D; BDO, APO, Wet-fix, Polyset, and Stearoyl chloride. Areas were reduced to only 70 percent or more in the following: Form W and Form P; and in Form S and Form D when prepared for adsorption study before drying. Details of these treatments will be described in a future publication.[7]

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PROCESS EVALUATION BY SCANNING ELECTRON MICROSCOPY [SUMMARY]

by

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The ultimate performance of a cotton fiber as a functional product depends on the chemical and physical state of the fiber, as well as its relation to the other fibers that surround it. It is probable in finishing processes that the nature of the fiber will be changed in some way. In fact, most treatments are designed to impart specific changes in the original properties of the fiber. However, certain undesirable changes are often brought about also. Many laboratory tests have been designed to measure pickups and add-ons, breaking strengths, and wrinkle-recovery angles as a measure of the success of a particular treatment. Such tests reveal little of what has happened to the individual cotton fiber during treatment, and it is often important to know of changes in surface features or damage to the fiber caused by the process.

The commercial development of the scanning electron microscope (SEM) within the past few years has made available a means of obtaining such information. The SEM is similar to the more conventional transmission electron microscope; however, a major difference is that thicker samples, such as whole fibers or swatches of fabric, can be viewed at focal depths great enough to survey their entire surfaces. It is possible to follow changes in the appearance of the fiber from the bale to the finished product.

To recognize changes in fiber structure it is necessary to understand at least basically the natural physical structure of the fiber. The cotton fiber has been described as a twisted, convoluted tube with a wrinkled surface, but it is somewhat difficult to actually envision this correctly. The SEM provides a natural three-dimensional picture of the fiber, and by coiling the fiber it is possible to see its entire length from base to tip. It is twisted and straight, rounded and flat; it is, in fact, highly nonuniform in structure. By using higher magnifications, the various types of twist, the reversals, and the wrinkled outer surface become evident. The fiber surface is continuous without naturally occurring cracks or breaks.

But does the fiber always reach the processor in this state? What happens to the fiber if at some time after the boll opens it is submitted to conditions of humidity and temperature such that is is attacked by fungus? Damage caused by fungus is shown by the SEM as breaks or cracks, usually horizontal or diagonal to the long axis of the fiber, which naturally leave the fiber weak.

If it is presumed, though, that the processor receives undamaged fibers, how well do they survive the chemical treatments given them in the production of consumer goods? Normal processes, such as scouring and bleaching carried out under controlled conditions, change the physical appearance of the fiber little except to produce a cleaner fiber surface. Mercerization swells the fiber to a more rounded cross section, and SEM pictures of mercerized fabrics indicate that mercerization is often very incomplete in that many fibers are not affected.

Chemical finishing can produce tremendous changes in functional characteristics of the fiber or fabric. Crosslinking tends to immobilize the fibrillar components and cause the fiber to be less resistant to abrasion. The normal pattern of fibrillar shredding characteristic of wet abrasion in native cotton fibers is changed to a pattern of peeling of sheets of fibrils.

Coating treatments designed to increase the abrasion resistance of chemically treated fabrics also have a pronounced effect on the utility of the fabric. It is expected that a thin coat of some soft polymeric substance spread evenly over the surface of a fabric will produce a somewhat stiffer fabric of increased abrasion resistance. However, the coating is seldom evenly spread over individual fibers and if it accumulates at cross points of warp and fill yarns, it very likely immobilizes the yarns. Chemical analysis may reveal that a large amount of coating material is present, but SEM observations show that many areas of the fabric surface may not be coated. In addition, the immobilization is likely to reduce the tear strength of the fabric.

Fabrics are also coated to produce weatherproof and rot resistant products. In such cases penetration of the coating through the fabric and adhesion to the fibers are of importance. Fabric cross sections prepared for SEM can show how far the resin has penetrated the fabric, as well as the depth of penetration into each yarn. Areas where the coating does not adhere to the yarns are also visible.

The application of heat is essential to many treating processes, but excessive heat can damage the fiber. This damage appears very similar to that caused by microbial attack.

It is evident that changes in surface features of fibers, yarns, and fabrics may have a marked effect on their functional character, and the ability to monitor such changes with the SEM as they occur in processing often helps in explaining any new or unexpected behavior they may exhibit. The advantage of the SEM in such evaluations of fabric, yarn, or fiber lies in the greater depth of focus and the possibility of surveying a larger area of the fabric.

SESSION II: Robert H. Barker, College of Industrial Management and Textile Science, Clemson University, Clemson, S.C., Chairman

SOME ASPECTS OF GRAFT PHOTOPOLYMERIZATIONS OF MONOMERS ONTO COTTON CELLULOSE
[SUMMARY]

by

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The expression 'photochemical grafting' is normally taken to imply initiation of a chain graft copolymerization process through the action of light. Photoinitiation can occur either by direct absorption and radical formation along the backbone of an existing polymer substrate or by the intervention of a sensitizer that first absorbs the light energy and in some way transfers this energy to the reacting molecules of the polymer substrate. In either case the free radicals produced in the backbone polymer are used to initiate the polymerization of a vinyl monomer.

The interest in photochemical grafting stems from the possibility that the copolymer products of cotton cellulose produced by this technique may have performance properties different from those prepared by using high energy radiation and other means. Experimental evidence would suggest that photoinitiated grafting in a heterogeneous system is predominantly a surface reaction (6). Thus, if photochemical copolymerization is to have any commercial promise, real differences must exist between the photopolymerization products of cotton cellulose and samples that contain similar contents of homopolymer deposited from solution.

The purpose of this paper is to review the major effects of ultraviolet light on cotton in direct and sensitized photolysis, since this is essential to understanding fundamental aspects of photochemical copolymerization, to examine techniques and limitations of photo-initiated grafting onto cotton cellulose, and to present some recent results on photopolymerization of reactive monomers onto cotton fabric.

Photolysis of cotton cellulose in the far-ultraviolet (2,000-3,000 A). – The action of light on cotton cellulose has been reviewed up to 1964 by Phillips and Arthur (14). Direct measurement of the absorption spectrum of cotton cellulose in the far-ultraviolet by the technique of diffuse reflectance spectroscopy was recently reported by Phillips. Absorption bands at ~ 2,150 A and 2,630 A, the latter being a broad diffuse shoulder, were observed in a variety of cotton samples. Prior to this observation, no evidence had previously been advanced to support a band absorption in cotton cellulose. The absorption at 2,630 A was also found to increase with time of photolysis, while the degree of polymerization decreased. It was felt that the absorption at ~ 2,630 A could be associated with solid state properties of cotton cellulose matrix. No such absorption was observed for the individual D-glucose monomer units in solution (13).

Flynn, Wilson, and Morrow (3, 5) reported a detailed study of the stoichiometry and kinetics of the several reactions taking place upon irradiation of cotton cellulose with 2,537 A light. A close stoichiometric correlation between quantum yields of hydrogen and aldehyde group formation was observed; and, a mechanism was proposed in which the alcohol groups of cellulose were photolyzed to carbonyl groups with the liberation of hydrogen. Also, it was assumed that CO and CO_2 in the gaseous products resulted from chain scission because of stoichiometric correlation between CO and CO_2 evolution with changes in the degree of polymerization. Differences in quantum yields for the various reactions among several cellulose samples – cotton sliver, cotton linters, and regenerated cellulose – were said to be caused by variations in physical properties rather than to variations in chemical constitution.

A postirradiation effect, that is, continued depolymerization and carboxyl group formation of the irradiated samples after the conclusion of the actual exposure, has been observed by several workers (3, 8, 17). Chain scission and carboxyl group formation that take place postirradiatively in the presence of oxygen has been said to result from the decay of long-lived oxyradicals on the C_2 and C_3 atoms of the anhydroglucose units of cellulose (4).

Photolysis of cotton cellulose in the near-ultraviolet (3,000-4,000 A). – The lower limit of ultraviolet rays reaching the earth is about 2700 A with most of the ultraviolet light reaching the earth falling between 3,500 and 3,900 A. While earlier reports indicate that light of wavelength greater than 3,400 A is unable to photolyze cellulose directly (2, 6), the fact that cotton cellulose degrades in sunlight is indisputable. The mechanism of photodegradation of cotton fabrics is little understood. It is generally felt that photolysis in the near-ultraviolet region is a photosensitized process rather than a direct photochemical reaction (16). The substance(s) responsible for the near-ultraviolet photosensitized degradation of cotton cellulose has not been identified.

The photolytic effect of near-ultraviolet light on the chemical and physical properties of fibrous cotton cellulose were reported by Reine and Arthur (15). With a highly intense ultraviolet light source of radiant energy with about 90 percent of the light in the 3,500 A range, the time of radiation was varied from 2 to 96 hours. At the end of 96 hr. there was a 16 percent loss in tensile strength of the irradiated fabric and measurable changes in carbonyl and carboxyl groups and chain cleavage of cellulose molecules. As in the case of photolysis of cellulose with 2,537 A light (5), the formation of carbonyl groups is the predominant change in cellulose on near-ultraviolet light photolysis. Similarly, a correlation between the number of chain cleavages and formation of carboxyl groups was observed in both cases. The main difference was that the effects with 2,537 A light on the properties of cellulose were several orders of magnitude greater than the effects of irradiation in the near-ultraviolet region (3,000-4,000 A).

Photosensitized reactions of cotton cellulose. – In a photosensitized reaction of cotton cellulose the primary action is absorption of light by an added substance, either an impurity or added treatment, which is called the sensitizer. This type of reaction is a secondary photochemical process since cotton cellulose is not known to absorb near ultraviolet or visible light.

The course of reaction after light absorption by the added sensitizer depends on the nature of the sensitizer. The photoexcited sensitizer may directly transfer its energy to a molecule of cellulose with subsequent localization of the energy in the anhydroglucose units. Localization of energy in the cellulose molecule initiates chemical reactions of the oxidative degradative type (1).

The photoexcited sensitizer may also interact with oxygen present to produce a reactive oxygen molecule that then attacks the cellulose polymer (9). The lowest energy ground state for oxygen molecules is a stable triplet state. Certain sensitizing substances can transfer their photoexcited state energies to oxygen to give excited singlet molecular oxygen. The very reactive oxygen molecule then attacks cellulose in a secondary photochemical process.

In other cases, radical oxidation of cotton cellulose can be initiated by sensitizers that are first photoexcited by light and react directly with cellulose by abstracting hydrogen to produce a reactive cellulose free radical. Among the best sensitizers for this type of reaction are the anthraquinoid vat dyes and related quinones. Active vat dyes absorb light of appropriate wavelength and are reduced to the leuco form by abstracting a hydrogen atom from cotton to give a reactive intermediate. Reoxidation of the leuco form of the dye by air generates the active dye, and the process is repeated; loss of fiber strength results.

Techniques of photoinitiated graft copolymerization onto cotton. – The methods reported for photochemical graft copolymerization of monomers with cellulose generally have been limited to a simultaneous irradiation procedure in which the cellulosic sample is immersed in a solution containing the monomer, solvent, and a sensitizer. With this technique, photopolymerization is usually accompanied by extensive homopolymerization. In fact, in many cases homopolymerization is the predominant reaction. Thus, the cellulose-polymer products resulting from the above method often consist of samples containing large amounts of homopolymer deposited from solution.

Geacintor and coworkers (6, 7) have grafted vinyl monomers onto cellulose films immersed in solutions of monomer and solvent with disodium anthraquinone-2, 6-disulfonic acid as photoinitiator.

Needles (12) reported that acrylamide and methyl acrylate are photografted onto a variety of natural and synthetic fibers, including cotton cellulose, when irradiated while suspended in monomer solutions with sodium riboflavin-5'-phosphate as sensitizer. The photopolymerization was accompanied by extensive homopolymerization. In contrast to riboflavin, disodium fluorescein caused photopolymerization on wool only.

More recently graft copolymerization of methyl methacrylate to cellulose with ultraviolet irradiation in the presence of hydrogen peroxide (10) and ceric ion (11) has been reported by Kubota and Ogiwara. Bleached sulfite pulp and bleached semichemical pulp were used as cellulose samples; and, the cellulose samples were suspended in an aqueous mixture of methyl methacrylate and hydrogen peroxide under nitrogen at 40° C. while irradiated with ultraviolet light.

In addition to the problem of extensive homopolymerization, which is associated with the methods reported in the literature for photopolymerization reactions with cellulose, practically no effort has been made to evaluate the cellulose-copolymer products.

Some recent results on photopolymerization onto cotton fabric. – Recently, we have found that significant photografting of monomers onto cotton fabric (80x80 printcloth) occurs over relatively short periods of irradiation (15 min.) utilizing a novel technique which is more applicable to commercial adaptation. In this method cotton fabric is first impregnated with an aqueous solution of monomer and sensitizer by padding at room temperature to a wet pickup of 185 to 200 percent. The treated fabric is then exposed to near ultraviolet light under a controlled atmosphere in a photochemical reactor at 40° C. After the reaction period, the modified fabric is washed successively in methanol and hot water. Deposited or grafted polymer was determined by weight gain and nitrogen analysis.

Methacrylamide was the monomer selected in these preliminary studies. In comparison with other reported studies on fibrous cotton cellulose where small weight gains were observed (8), our method with aqueous solutions of methacrylamide (10 percent) and photolysis times as low as 15 to 90 minutes resulted in weight gains as high as 7 to 18 percent. The degree of photochemical copolymerization was dependent on time of photolysis and concentrations of monomer. Conducting the reaction in an oxygen atmosphere also affected the extent of copolymerization.

Evaluations of fabric properties such as breaking strength, elongation at break, tearing strength, abrasion resistance, stiffness, and wrinkle recovery angles were made on the products to test the possibility that photochemical grafting can be used to improve the properties of cotton fabric.

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ACRYLAMIDE -- MODIFIED SILICONE FINISHES FOR COTTON
[ABSTRACT]

by

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Methyl hydrogen silicone reacts with activated olefins in the presence of alkaline catalysts to yield modified silicones of varied structures and properties. With vinyl sulfones, the silicone appears to undergo addition to form sulfonylethyl silicones. With acrylamide, reaction at the amide group occurs first, with hydrogen being evolved, and at elevated temperatures a crosslinked silicone-amide copolymer is formed. The base-catalyzed application of acrylamide, N-methylolacrylamide and other N-substituted acrylamides to cotton in the presence of methyl hydrogen silicone is described, and certain physical properties of treated fabrics, such as water repellency, wrinkle resistance, strength, and softness, are characterized.

CHEMICAL MODIFICATION OF COTTON AND ANION EXCHANGE COTTONS WITH PROPANE SULTONE IN ORGANIC SOLVENTS
[SUMMARY]

by

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(Presented by T. L. Ward)

A large amount of work is reported in the chemical and patent literature regarding the cyclic esters of sulfonic acids, which are known as sultones. Sultones react with compounds containing one or more active hydrogen atoms linked directly to oxygen, nitrogen, or sulfur. These reactions often require an alkali metal cation as catalyst. However, some have reported on the direct reaction of sultones with amines.

The literature reports on the reaction of sultones with cellulose to form a product with improved dye receptivity and with built-in acid groups capable of catalyzing subsequent reactions of cellulose with conventional crosslinking reagents. Earlier work was with cotton and sultones in aqueous solutions catalyzed with sodium hydroxide. Reactions of sultones with cotton in nonaqueous media and with cotton containing built-in amine or carboxylic groups as catalytic sites have not been reported.

In the present study, sodium cellulosate prepared by reacting cotton fabric with sodium alkoxide in anhydrous alcohol was subsequently reacted with propane sultone in several organic solvents. Results were compared with those obtained in an aqueous system. Cotton fabric modified to contain tertiary amine groups (DEAE cotton) another modified to contain primary amine groups (aminized cotton), and one modified to contain carboxyl groups (carboxymethyl cotton), were also used to assess the reactivity of propane sultone with cottons containing these reactive groups.

Sodium cellulosate prepared, stored, and used in nonaqueous solvent reacted readily with propane sultone. About three fourths of a milliequivalent of sulfur was added per milliequivalent of sodium present in the sodium cellulosate. Reaction between sodium cellulosate and propane sultone in tertiary butanol reached equilibrium with 3 percent sulfur added in about 1 hour at 50° C. Cotton in an aqueous system added 1 percent sulfur in the same time at 50°. The reaction with sodium cellulosate proceeds in acetone or in dimethylformamide at a slower rate. Although it may be possible to add as much sulfur to cotton by use of the propane sultone in aqueous sodium hydroxide, the nonaqueous procedure produces a more rapid reaction at a relatively lower temperature. Since sodium cellulosate in fabric form has been prepared with up to 4 meq of sodium per gram of product, up to about 3 meq per gram of product (10 percent) of sulfur can be added to fabric.

Diethylaminoethyl (DEAE) cotton was prepared by reacting sodium cellulosate with 2-chloroethyldiethylamine in t-butanol. In one series, the DEAE fabric was kept in the free amine form by washing in t-butanol only and subsequently reacting it with the sultone in t-butanol. For comparative purposes, some of the DEAE fabric was removed from t-butanol, washed with water, and air dried before being reacted with the sultone in t-butanol. The free-amine form added in 20 hours 2.34 percent sulfur from a 10 percent solution of propane sultone in t-butanol at 50° C. The water-washed sample with similar nitrogen content added only 0.83 percent sulfur. Use of freshly prepared DEAE cotton in the free-amine form gave a several-fold increase in reactivity with the sultone over that obtained with the water washed DEAE cotton in several organic solvents.

A commercially available DEAE anion exchange cellulose in the powder form reacted with propane sultone to add the same amount of sulfur per meq. of nitrogen as did a water washed DEAE cotton in fabric form.

DEAE cotton reacted for 20 hours at 50° C. with the propane sultone without added catalyst in methanol, DMF, or t-butanol. Reaction was best in t-butanol (2.34 percent S), poorest in methanol (0.91 percent), and intermediate in DMF (1.60 percent).

DEAE cotton even in the amine form does not react so rapidly with propane sultone in t-butanol as does sodium cellulosate. DEAE cotton in the free amine form adds more than a milliequivalent of sulfur per milliequivalent of nitrogen. The DEAE cotton prepared nonaqueously and washed, stored, and used in tertiary butanol still contains some sodium ions left as unreacted sodium cellulosate. About one-third of those present originally in the sodium cellulosate remain. Therefore, DEAE cotton has about 0.5 meq. of sodium per gram of product that can cause reaction with the sultone. In addition, the DEAE has 0.61 meq. of nitrogen per gram of product that can react directly with the sultone. The amount of sulfur added is about what would be expected to result if reaction occurred at the amine groups and also at the cellulosate sites.

Aminized cotton, which contains primary amine groups rather than tertiary amine groups as does DEAE cotton, is not nearly so reactive with propane sultone in t-butanol or DMF. In a 10 percent solution of propane sultone in t-butanol at 50° C. for 20 hours, only 0.14

percent sulfur added. In methanol, under the same conditions of time and temperature, 1.26 percent sulfur added. The latter represents about 0.40 milliequivalents of sulfur added per milliequivalent of nitrogen in the aminized cotton.

Aminized cotton cannot be prepared, stored, and used in a completely nonaqueous system with the chemicals commercially available for the preparation. This means that the aminized cotton used in this study had been washed with water and air dried prior to its reaction with the sultone. DEAE cotton handled in a similar manner reacts with the sultone in methanol to give a product with 0.30 milliequivalents of sulfur per milliequivalent of nitrogen.

To determine if the amine group attached to the cotton acted as a catalyst rather than as a reaction site, we tried external base catalysis of the reaction of the sultone with unmodified cotton. No reaction of cotton with propane sultone occurred whether the external base was padded on the fabric prior to its immersion in the sultone solution or placed directly into the solution.

One reason that methanol increases reaction with the aminized cotton but decreases the reaction with nonaqueous DEAE-cotton is that the methanol quickly exchanges the sodium ions still present as sodium cellulosate in the nonaqueous DEAE-cotton. This leaves only the amine groups to react with the sultone.

Carboxymethyl cotton and propane sultone did not react. The carboxymethyl cotton was used in the salt form and in the acid form. Others have reacted propane sultone with a number of monocarboxylic acids. In carboxymethyl cotton, the reaction may be impeded by hydrogen bonding between the carboxyl group and a nearby cellulosic hydroxyl.

Tertiary butanol is the solvent of preference except for aminized cotton. About 10 percent of propane sultone in the solvent seems to be the optimum concentration. A temperature of 50° C. for approximately 1 hour is sufficient in most instances.

The Monsanto wrinkle-recovery angles are increased a modest 12 to 15 percent for the sodium cellulosate after reaction with the sultone but are not changed for the DEAE cottons. Subsequent reactions of the sultone product with various crosslinking agents result in improved wet and dry wrinkle recovery.

REVERSIBLE CREASING STUDIES IN COTTON CROSSLINKED WITH N-METHYLOL FINISHING AGENTS

[SUMMARY]

by

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(Presented by Stanley R. Hobart)

Fabrics that are permanently pressed are currently enjoying great popularity. However, they would have greatly enhanced utility if they had the ability to be altered to new permanently pressed shapes. Thus, if crosslinks responsible for holding the fabric in its original flat or creased state could be broken and reformed with the fabric in a new configuration, an "alterable permanent press" fabric would be possible.

It has recently been shown by Soignet and others (Textile Res. Jour. 39: 780-787 (1969)) that the acid salts of diethylaminoethyl (DEAE)-substituted cotton act as an *in situ* catalyst for the reaction with N-methylol finishing agents. Therefore, it should be possible to break and reform crosslinks in cotton fabric at will using this type of reagent-catalyst system. It is the purpose of this paper to report the conditions required to accomplish this.

This study covers two levels (0.8 and 1.2 percent nitrogen contents) of DEAE-substituted cottons and six N-methylol finishing agents: dimethylolethyleneurea (DMEU), *tris*-(methoxymethyl)melamine (TMM), *bis*-(methoxymethyl)urea (Me U-F), dimethyloluron (Uron), dimethyloldihydroxyethyleneurea (DMDHEU), and dimethylol methyl carbamate (DMMC). The DEAE cottons were found to react with the N-methylol finishing agents much less readily than cotton itself. It was necessary to use an added external catalyst (zinc nitrate) in addition to the DEAE acid salt and reagent concentrations from 25 to 50 percent greater than those used with untreated cotton to obtain comparable add-on's with the DEAE cottons. The order of reactivity for the N-methylol finishing agents used was as follows: DMEU > TMM = Me U-F > Uron > DMDHEU > DMMC.

The creasing of these fabrics was carried out by first converting the DEAE group to its acetic acid salt, rinsing free of acid, blotting off excess liquid, clamping in the creased position between glass plates, and heating at 160° C. for 6 minutes. Sharp creases (AATCC rating of 5) were obtained in all fabrics investigated, although durable creases were not obtained in every case. Durability was measured by rating the creases after five home washing and drying cycles. In some cases, ratings of 3 to 4 were encountered after the launderings, while in others the creases were essentially removed. Generally, the samples of DEAE cotton containing 1.2 percent nitrogen were slightly better in producing durable creases than those containing 0.8 percent nitrogen. In an attempt to compare finishing agents, it was observed that the same general order of reactivity prevailed that was found in the reactivity scale listed above. That is, DMEU was more reactive with DEAE cotton and also formed durable creases more readily. DMEU was, however, the most readily acid-hydrolyzable of the finishes used.

Conditioned wrinkle recoveries greater than 280° (twice warp) were obtained for all but two (one Me U-F and one Uron) of the finishes on DEAE cotton, and all remained at 272° or higher after the creasing process and laundering. Fabrics treated with DMEU were again the leaders in this regard, the majority being 292° or higher initially.

Nitrogen and formaldehyde analyses were carried out on all of the samples before and after the thermal creasing treatment. Changes in nitrogen contents were observed as a result of the heating and washing treatments, whereas the DEAE controls lost essentially no nitrogen. Therefore, catalyzed reversibility of some of the N-methyl linkages with cellulose is noted. Further substantiation of this is seen in those samples that possess the higher levels of finishing agent where relatively larger losses of nitrogen are noted. The nitrogen that is lost must have been associated with non-crosslinking cellulose reaction since little or no loss in conditioned wrinkle recovery is observed. Nitrogen/formaldehyde ratios are calculated for all the samples and are discussed.

The introduction of creases into wrinkle-resistant fabrics indicates that N-methyl linkages with cotton cellulose can be cleaved and that once separated from one cellulosic hydroxyl group, the N-methylol group may be reacted at another site. Furthermore, the presence of the amine salt in the fabric substrate has been shown to be effective in catalyzing the breaking and reforming of the ether linkages on heating. The fact that these salt groups are built into the fabric prior to finishing makes them properly positioned at the site of the ether linkage so that catalysis of both the forward and reverse reactions is not prevented by steric factors.

CATALYSIS OF CROSSLINKING REACTIONS IN COTTON BY POLYCARBOXYLIC ACIDS [SUMMARY]

by

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(Presented by W. E. Franklin)

This paper describes experiments on the use of polycarboxylic acids (PCAs) as catalysts and coreactants in crosslinking and recuring reactions in cotton cellulose fabrics. The objective of this research is to provide a cotton fabric having the desirable properties of a durable press fabric, but that can be durably creased or uncreased by a pressing or other recuring operation. Such a fabric would make it possible to alter durable press garments in the home or in the retail outlet and to correct certain errors in the manufacturing process for durable press fabrics and garments.

Recurable, crosslinked cotton fabrics have been made with crosslinking agents that dissociate when heated. Examples of such agents are Diels-Alder adducts, aryl carbamates, and polycarboxylic acids. Fabrics treated with these agents did not have the high resilience required of durable press fabrics. A more acceptable recurable, crosslinked cotton fabric has been made by treating a cotton fabric containing covalently bonded quaternary ammonium hydroxide groups with divinyl sulfone. This fabric has good performance and recuring properties, but the process for making it was long and required many steps.

Polycarboxylic acids can be caused to react with cotton cellulose fabrics by a pad-dry-cure process. Under appropriate conditions, ester crosslinks are formed, but the reaction is not complete and free carboxyl groups remain in the fabric. Many of these acids containing three or more carboxyl groups are readily soluble in water to give moderately acidic solutions. It therefore seemed likely that these polycarboxylic acids could be used as catalysts and coreactants in crosslinking reactions of cotton cellulose fabrics with standard methylolamide reagents and that the resulting fabrics would contain covalently bonded, acidic groups that would catalyze recuring reactions in these fabrics.

The methylolamide crosslinking agent chosen for this study was dimethyloldihydroxyethylene urea (DMDHEU). Three polycarboxylic acids (PCAs) were chosen for this study because of their high water solubility and because they are, or can be, produced at moderate price. These were citric acid, cyclopentanetetracarboxylic acid (CPT), and tetrahydrofurantetracarboxylic acid (THFT). Two other acids were also used despite their low water solubility because of interesting results in preliminary experiments. These were nitrolotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA).

The padding solution contained 12 percent DMDHEU, 2 percent emulsified polyethylene softener, 0.1 percent non-ionic wetting agent, and 3, 6, or 12 percent of the PCA. Only 3 percent of NTA or EDTA and only 4 percent of $MgCl_2.6H_2O$ were used. The fabric, an 8 oz./yd. khaki twill, was padded to 70 percent wet pickup, dried at 70° C. for 8 min. and cured at 160° for 8 min. These conditions were chosen to give good wrinkle recovery angles (WRAs) and to insure the formation of ester bonds between the PCAs and cotton cellulose.

Textile properties of the DMDHEU-PCA fabrics. – The soluble PCAs were efficient catalysts for the reaction of DMDHEU with cotton cellulose, as shown by the high conditioned WRAs (295°-305°, W+F) of these fabrics. There was some indication of a trend toward slightly higher WRAs as the concentration of the PCA increased, but 6 percent of the PCA was apparently enough to ensure complete cure in all the fabrics. The less soluble PCAs, NTA and EDTA, were less efficient as curing catalysts, giving conditioned WRAs of 286° and 280°. The $MgCl_2$ control had a conditioned WRA of 301°.

The abrasion resistances (Stollflex life) of the fabrics treated with the soluble PCAs were moderately low, as is usual in cotton fabrics with WRAs in the range of 300°. However, the abrasion resistances of all of the PCA fabrics except the 6 and 12 percent THF fabrics were significantly higher than those of the $MgCl_2$ catalyzed fabrics. The abrasion resistances of the NTA and EDTA fabrics were very high (126 and 228 percent of that of the unmodified fabric). The low abrasion resistance of the 6 and 12 percent THF fabrics was probably a result of the high acidity (pH 1.7 and 1.3) of these pad baths. The breaking strengths and tearing strengths followed a similar pattern, with the PCA fabrics (except the 6 and 12 percent THFT fabrics) moderately higher than the $MgCl_2$ control, and the NTA and EDTA fabrics significantly higher. In summary, citric acid, CPT, and 3 percent THFT, which give pad baths with a pH between 2 and 3, give equivalent WRAs and somewhat better strength retention when compared with $MgCl_2$, while NTA and EDTA give lower WRAs and much better strength retention.

Recuring of DMDHEU-PCA fabrics. – The recuring properties of the DMDHEU-PCA fabrics were investigated by measuring the durability of creases introduced in samples of the fabrics by a standard heat treatment.

Small (2"x3") pieces of the fabrics were soaked in water, folded, and placed on a preheated cloth surface. The folded fabric samples were then pressed with an electric iron that was controlled by a thermocouple placed between the sides of the fabric sample. In this procedure, the temperature rose over about 2 min. as the water evaporated and then held steady at $160\pm 1^\circ$ C. for 3 min. (a total pressing time of 5 min.). After this pressing operation, all fabric samples had crease appearance ratings of 5 on the AATCC scale (from 0–no crease to 5–best crease). The creased fabric samples were rinsed in hot water for 1 hr., then stapled to towels and subjected to five home laundering cycles. The samples were again rated for crease appearance to measure the durability of the creases formed in the pressing or recuring operation. In this crease durability test, the unmodifed cotton controls retained very poor creases (AATCC rating 0.5) and the fabrics cured with $MgCl_2$ had almost no crease (AATCC rating 0.1). The fabrics treated with the soluble PCAs (citric, CPT, and THFT) retained very good creases (AATCC rating 4.0 or better), and the fabrics cured with NTA and EDTA had poor creases (AATCC rating 1.0).

Samples of the fabrics were treated with very dilute hydrochloric acid or acetic acid in order to convert all the free carboxyl groups to the acid form and then thoroughly rinsed with distilled water and pressed as before. The durability of creases pressed into the fabrics cured with the soluble PCAs was unaffected by the acid treatment, but the fabrics cured with NTA and EDTA retained good creases (AATCC rating 3.5) when they were pressed after the acid treatment.

Samples of the DMDHEU-PCA fabrics were treated with very dilute sodium hydroxide to convert the free carboxyl groups to the sodium salt form and then thoroughly rinsed with distilled water. None of these fabrics accepted durable creases in the standard pressing operation. The fabrics in the sodium salt form were further treated with magnesium chloride to convert them to the magnesium salt form. These magnesium salt fabrics also failed to accept durable creases in the standard pressing operation. In summary, the DMDHEU-PCA fabrics accepted durable creases in a recuring operation if the free carboxyl groups were in the acid form, but the unmodified and magnesium chloride controls and the DMDHEU-PCA fabrics in the salt form did not show evidence of recuring in the same pressing operation.

The following table summarizes the results described in this article:

Polycarboxylic acid or catalyst	pH of bath	Add-on (percent)	WRA (°W+F) Conditioned	WRA (°W+F) Wet	Strength retention (pct. of unmodified control) Abrasion	Break	Tear	AATCC crease rating after 5 min. pressing and 5 laundering cycles Wash only	Acid	Na salt	Mg salt
3 percent citric	3.0	6.4	291	266	74	62	74	4.1	—	—	—
6 percent citric	2.5	6.6	295	269	45	61	66	4.1	—	—	—
12 percent citric	2.1	7.8	300	277	37	56	57	4.0	4.0	0.6	0.8
3 percent CPT	2.9	5.4	274	250	172	66	86	4.0	—	—	—
6 percent CPT	2.5	9.1	306	276	30	63	50	3.6	—	—	—
12 percent CPT	2.0	10.4	303	268	32	61	—	4.8	4.1	0.5	1.0
3 percent THFT	2.3	7.0	302	271	46	62	69	4.1	—	—	—
6 percent THFT	1.7	7.8	309	271	17	53	—	4.0	—	—	—
12 percent THFT	1.3	11.0	300	291	8	48	50	4.0	4.3	0.5	0.0
3 percent NTA	2.3	4.9	286	275	126	68	80	0.8	3.6	0.0	0.1
3 percent EDTA	3.7	3.9	280	251	228	71	86	1.0	3.3	0.5	0.5
4 percent $MgCl_2 \cdot 6H_2O$	5.1	4.0	301	267	17	52	57	0.0	1.8	0.0	0.1
Unmodified control	—	—	—	169	178	100	100	0.6	0.5	0.5	0.5

SOLUTIONS OF BENZYLTRIMETHYLAMMONIUM HYDROXIDE IN LIQUID AMMONIA OR AMIDES AS A MEANS OF PUTTING SHAPE IN COTTON TEXTILES

[ABSTRACT]

by

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Concentrated (35 to 40 percent) aqueous solutions of this quaternary base were previously shown to convert cotton to a decrystallized, plastic state in which false twist could readily be imparted to yarn or creases set in fabric. Removal of the agent permitted recrystallization of the cellulose in the new imparted shape. It is now found that dilute (5 percent) solutions of the quaternary hydroxide in liquid ammonia, hydraxine, or amines are also effective in plasticizing cotton. A synergism is evident between the quaternary ammonium hydroxide and the ammonia or amine, since neither liquid ammonia nor dilute aqueous benzyltrimethylammonium hydroxide are by themselves effective. The addition of urea to liquid ammonia increases the solubility of the quaternary base in this solvent.

TEXTILE MODIFICATION IN A CORONA FIELD

by

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ABSTRACT

Corona treatment of wool and mohair fibers produces polar sites, some of which have been identified as sulfonic acid groups on or very near the fiber surface. Fiber friction and wettability in water increase. Electrostatic behavior is altered and soil repellency and resistance to felting shrinkage are increased. Treatment with a cationic surfactant reverses effects of corona treatment on wettability, friction, and shrinkage. Chlorine-corona treatment of cotton produces a C-Cl Covalent bond and alters the structure of the primary wall. Wool and cotton fiber friction and roving cohesiveness are very high immediately after corona treatment but diminish in a few hours to a level somewhat above the original value. Improved mohair carding and wool and cotton spinnability result, and the tensile strength of wool, mohair, and cotton yarns and of blended yarns is increased. Yarn hairiness is decreased. Cotton fabric abrasion resistance is increased.

INTRODUCTION

A plasma, or partially ionized gas, can be conveniently produced by any of several electrical discharge techniques. The corona discharge, a type of silent or nondisruptive discharge has a marked advantage in simplicity and produces a low temperature plasma containing numerous tiny thermal sparks. Earlier studies have shown (2) that if textile fibers are present, the highly reactive species can alter their physical properties in several beneficial ways. Reaction rate, however, is slow, nonuniform, and ineffective with certain textile fibers. We have attempted to improve the treatment effects obtained and the results are described below.

RESULTS

We first tried to find optimum conditions for treating wool and mohair. Improved resistance to felting shrinkage was obtained and fiber burning eliminated by raising the temperature to 85° C. or above (8). Increasing frequency and voltage to about 2,000 Hz and 17.5 kV., respectively, and injecting dilute chlorine gas into the corona cell (6) further accelerated the reaction. Some of the molecular species which may be introduced or formed in the corona field are shown below (4). The oxides of nitrogen are produced at high field strength. Only activated species react with the fibers inasmuch as no reaction is detected during similar treatments without the corona field.

SPECIES IN CORONA FIELD
(with air-moisture-Cl_2 present)

O_2	H_2O	O_2^-	O_2^+	$\cdot O$
O_3	H_2O_2	O_3^-	O_3+	$\cdot OH$
		OH^-	H^+	
N_2	HNO_3	N_2^-	N_2^+	$\cdot N$
N_2O_4	HNO_2	NO_3^-		
N_2O_5	Cl_2	Cl^-		$\cdot Cl$
N_2O	ClO_2			
	Hcl			

Reaction is apparently limited to the cuticle of the wool or mohair fibers (8). Kassenbeck[1] has found that the depth of penetration into the cuticle is only about 100 Å. However, Makinson (5) through micromanipulation, has evidence of considerably deeper penetration. Scanning electron microscopy shows the surface of many corona-treated fibers unchanged, although some fibers have a few pock marks and roughened scale edges possibly resulting from the treatment.

Corona treatment makes the surface of wool and mohair fibers more polar and therefore markedly increased their wettability by water. Their higher surface energy and more polar surface can also be shown by the red color produced when mohair fibers are exposed to a colorless solution of the dye rhodamine-b in toluene. Untreated fibers, on the other hand, remain colorless in the toluene solution because of their relatively nonpolar surface. Such colorless test solutions are conveniently made by extracting a dilute aqueous solution of rhodamine-b with toluene. Rhodamine-b remains colorless in the toluene extract as long as nonpolar materials are present, but turns red (the dye itself becomes polarized) in the presence of polar compounds, including hydrogen donors (3).

The wicking behavior of a thin strand of mohair fibers is markedly altered by corona treatment. When treated and untreated wicks of mohair fibers are placed over the edge of a beaker containing toluene and water (fig. 1), the lower water layer is siphoned out by the hydrophilic corona-treated wick, while toluene is siphoned out by the oleophilic untreated wick. Evidence that the polar sites are negatively charged was obtained from

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[1] Kassenbeck, P. Personal communication.

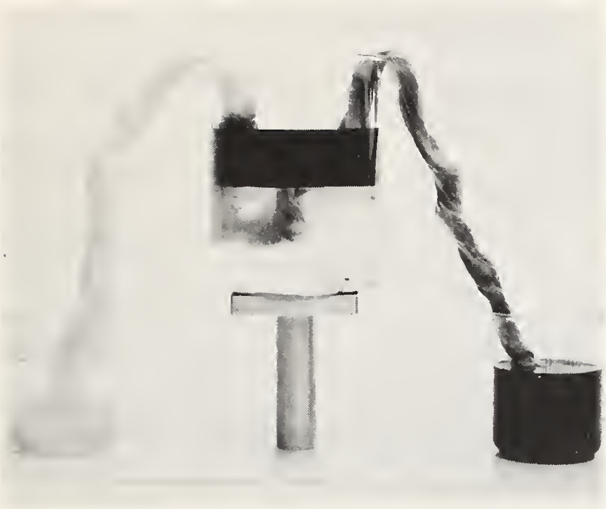

Figure 1. Wicks of untreated and corona treated 28's mohair in toluene layered over water.

the following experiment. If a cationic surfactant is dissolved in the water, the treated wick siphons toluene instead of water. Apparently the cationic "head" of the surfactant attaches to negative sites on the surface, with the result that the exposed hydrocarbon "tails" make the surface relatively nonpolar.

Some of the negative sites have been identified as sulfonic ($-SO_3H$) acid groups through the new ESCA (electron spectroscopy for chemical analysis) technique. This supports the hypothesis that cystine is oxidized by the treatment and that this is the predominant reaction. The increased electronegativity of the surface is also expressed by change to a more negative position in the triboelectric series (1). Corona-treated fibers can be made electrostatically neutral to various insulators such as leather, rubber, and others by controlling the degree of treatment. This effect may have practical application for wool or mohair carpets. Soil repellency is increased by corona treatment because soils are generally negatively charged.

When cationic surfactant is added to treated mohair fibers, their friction is reduced to that of untreated fibers—probably for the reason given for the wicking reversal.

Resistance to felting shrinkage in wool and mohair is increased (6, 8, 9) by corona treatment. Again, this effect can be reversed by adding a cationic surfactant at low pH. ESCA studies also revealed that the corona treatment of cotton in dilute chlorine gas produces C-Cl covalent bonds.

Since substantial quantities of corona-treated fibers were needed to study processing behavior and fabric properties, pilot scale equipment was required for the treatment of top or sliver, or raw stock. We therefore developed a continuous treatment pilot scale corona reactor with these required features (9) (fig. 2).

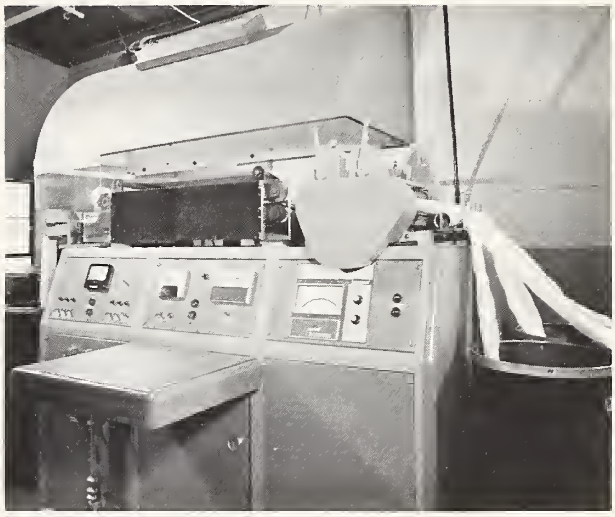

Figure 2. Corona reactor for continuous treatment of top or sliver.

The fiber friction and cohesiveness of mohair treated as raw stock are increased with no change in its highly desirable luster. Processing behavior is improved (10) so that the mohair can be efficiently carded on a woolen card. The spinnability of wool and cotton (7) is increased. Soft twist yarns may be produced with no loss in tensile strength. In one experiment with wool the spindle speed could be increased 47 percent, from 6,000 to 8,800 r.p.m. Wool, mohair, and cotton tensile strength are improved 12, 31, and 26 percent, respectively, and the strength of blend fabrics is increased if one of the components is corona treated. Yarn hairiness is decreased. Fabrics with excellent machine washability (9) can be made from corona-treated mohair. On the other hand, we can make wool garments adequately shrinkproof for hand washing but not for machine washing. Abrasion resistance of wool fabrics is not improved and in some treatments it is impaired, but that of cotton fabrics is increased about 50 percent. Dye-fastness of fabrics is not affected, but the rate of dye uptake is sometimes increased.

Fabric hand is somewhat impaired by corona treatment, but this loss can be restored by applying a suitable softening agent. The softening agent will not impair the shrinkage control because this effect occurs only at low pH. The hand of wool and cotton is harsh immediately after treatment but, interestingly, it softens gradually. Investigation of fiber friction and cohesiveness (11) disclosed high initial values that diminish rapidly to a stable value within a few hours and this residual cohesiveness is responsible for the increased yarn strength which was observed. The initial cohesiveness of cotton roving after treatment is extremely high, 420 percent above that of untreated roving; cohesiveness of wool roving is similarly increased 230 percent. This short-term increase probably can be used to improve spinning even more than treatment followed by delayed processing. If a method could be found to "freeze in" the initial high cohesiveness, strikingly higher values of yarn strength would most likely be achieved.

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PROCESSES FOR THE CONTINUOUS AMMONIA MERCERIZATION OF TEXTILE MATERIALS

[SUMMARY]

by

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(Presented by Timothy A. Calamari, Jr.)

A specially designed chainless mercerizer has been developed which makes it possible to carry out the ammonia mercerization of cotton and cotton/polyester blends under tension on a continuous basis. Through suitable modifications, woven goods, knitted goods, or yarn may be processed without difficulty.

Samples of rope bleached all-cotton and 50/50 cotton/polyester sheeting were ammonia mercerized on the SRRL equipment with practically no length or width shrinkage. When chemically crosslinked for durable press properties and enhanced dimensional stability, ammonia mercerized samples exhibited significantly better physical properties than either the nonmercerized or the conventionally caustic mercerized crosslinked controls.

Through the use of a feed roller and a floating spreader bar, it has been possible to process plain knit cotton jersey in tubular form on the mercerizer. The ammonia treatment of plain knits in tube form was necessary since the processing of a single thickness is complicated by the stresses and strains present in such a construction that cause varying amounts of edge curl distortions. Although plain knit constructions experience some course shrinkage when ammonia mercerized in this manner, there is a compensating elongation of the wale, which reduces the total area shrinkage. By use of a suitable feed mechanism, such as expander rolls, it should be practical to reduce course shrinkage further. When crosslinked for improved dimensional stability the ammonia mercerized samples had a much more stable configuration to laundering than a nonmercerized crosslinked control. Furthermore, the mercerized then crosslinked samples had Mullen bursting strengths much higher than those of the crosslinked controls and almost as high as that of an untreated control.

Either a single end or multiple ends of yarns may be processed on the mercerizer by using suitable letoff and takeup mechanisms. For our purposes, a skein winder is used as a feed device to introduce the yarns into the mercerizer under constant tension. Tension is adjusted so that it is sufficient to cause a slight increase in length after mercerization. Under these conditions, a significant increase in breaking strength is observed with little change in tenacity, elongation to break, or dye substantivity.

In addition to the improved physical properties already discussed, the luster of both woven and knitted goods as well as that of yarns is considerably improved by ammonia treatments on the SRRL mercerizer. Preliminary results have been encouraging and have indicated that further development could make this mercerizer suitable for use by the textile industry.

IMPROVEMENT OF STRENGTH IN DURABLE-PRESS COTTON KNITTED FABRICS THROUGH FABRIC MERCERIZATION
[SUMMARY]

by

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(Presented by B. A. Kottes Andrews)

Knitted cotton fabrics were treated with increasing concentrations of sodium hydroxide ranging from 5 to 25 percent. It was found that mercerizing strength sodium hydroxide (20 percent or higher) produced fabrics with increases in bursting strength. With these strength increases, up to 90 percent of untreated, unmercerized fabric strength was retained after crosslinking with 6 percent dimethylol dihydroxyethylene-urea for dimensional stability and durable-press properties. Percent moisture regain of these samples was increased from 4.6 to 6.1 percent. Spectroscopical examination showed 25 percent Cellulose II present in the mercerized samples that had barium numbers above 175. Fabric stiffness, which was increased undesirably by the mercerization, did not persist through a subsequent crosslinking treatment. Dimensional stability and resistance to flat abrasion were unchanged by crosslinking from that of crosslinked unmercerized fabric.

The stage at which tension was applied during the mercerization was varied to study the effects on properties of the mercerized fabrics after crosslinking. Tension, to restretch the fabric up to 89 percent original dimensions, was applied (1) immediately after slack mercerization; (2) after rinsing, either in hot water alone or in a dilute sodium hydroxide solution followed by hot water; (3) after a neutralizing rinse in 5 percent acetic acid; and (4) after a final cold water rinse.

Bursting strength retention after crosslinking of fabric mercerized at original dimensions was greater than that of mercerized fabric to which tension was applied after complete removal of sodium hydroxide but equal to that of fabric tensioned while some sodium hydroxide was still present. Fabrics treated for durable press could be produced with 75 to 95 percent initial fabric strength retained.

Resistance of the untreated fabric to flat abrasion in the Stoll test is improved by tensioning during mercerization. Although some of this increase is lost on subsequent crosslinking, the net effect is a 90 percent gain over that of the unmercerized crosslinked fabric. Inclusion in the crosslinking bath of a reactive hand-building agent, polyvinyl alcohol, improves the abrasion resistance of unmercerized fabric. This agent produces even greater improvements in resistance to flat abrasion of mercerized fabric up to 150 percent of that of untreated, unmercerized fabric. Other properties are equal to those of crosslinked unmercerized fabric. Chemical effects of tensioning after initial slack mercerization include increased conversion of Cellulose I to Cellulose II.

The level of polyacrylate and polyurethane additives to crosslinking baths necessary to optimum durable-press properties of mercerized knitted fabrics remains the same as for unmercerized fabrics. If the reactive hand-building agent, polyvinyl alcohol, is used the level can be reduced. Durability to damage in 50 home laundry cycles and retention of pressed-in crease and durable-press appearance of postcured knitted trouser cuffs fabricated from mercerized fabric is very good.

A LOW TEMPERATURE CATALYST SYSTEM FOR DP FINISHING
[SUMMARY]

by

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(Presented by Russell M. H. Kullman)

A catalyst system has been developed that can be used with dimethylol carbamates, cyclic urea agents, or formaldehyde for durable press finishing of cotton and polyester/cotton fabrics under mild curing conditions. A postcure process also has been devised whereby durable creases and smoothness are produced with treatment conditions markedly less severe than those of the present, widely practiced technique. Details of the research leading to these findings are given in this presentation.

Mild-cure finishing, first disclosed at the 8th Cotton Utilization Research Conference in 1968, imparts high levels of wet and dry (conditioned) wrinkle resistance to cotton. Fabric was impregnated with a suitable crosslinking agent and a strongly acidic catalyst, then heated under mild curing conditions without prior drying, and afterwashed. Although exact curing conditions vary with fabric weight and structure and with the efficiency of the equipment, a cure of 7 minutes at 60° C. produced a good finish on cotton print cloth. Dimethylol carbamates and strong mineral acids, particularly hydrochloric acid, worked well in the process. Because of the combination of high wet and dry wrinkle resistance, the finished fabrics dry smoothly after either tumble drying or line drying. In further work, the process was made more rapid. Treatments of 2 minutes at 100° were demonstrated. However, there was still great reluctance by American finishers to adopt the process. They were concerned that the strong mineral acid catalyst could damage plant equipment and could cause excessive strength losses in the finished fabric.

In the present work, other catalysts for use in mild-cure finishing were sought. Weak acids do not provide adequate catalysis for this process. However, mixtures of certain salts and of salts and acids have been shown recently to provide strong catalysis for other finishing techniques and were considered. Of various combinations tried, mixtures of ammonium chloride and phosphoric acid or certain organic acids were promising. These catalyst mixtures were investigated more fully and developed as alternatives to hydrochloric acid in mild-cure finishing.

The effects of interaction of catalyst parameters and other treatment variables were established. Samples of cotton printcloth were impregnated with a solution containing 15 percent dimethylol methyl carbamate (DMMC) and 2 percent of an equimolar mixture of ammonium chloride and phosphoric acid, heated in a circulating air oven for various combinations of time (3 to 10 min.) and temperature (60° to 100° C.) and washed. Chemical analyses indicated that some reaction had taken place, but there was little change in conditioned wrinkle recovery and in breaking strength by treatments below 100°. The ammonium chloride/phosphoric acid mixture did, however, provide sufficiently strong catalysis to give a wrinkle resistant finish at 100°. The catalysis is obviously weaker than that of hydrochloric acid which produced high levels of wrinkle resistance with curing at 60° and moderate levels even at 40°. However, the catalysis provided by the ammonium chloride/phosphoric acid mixture is considerably stronger than that of the Lewis acid salts (zinc nitrate, zinc chloride, and magnesium chloride) that are commonly used in conventional pad-dry-cure finishing. Mixtures of ammonium chloride with other acids—citric, oxalic, tartaric, and trichloroacetic—likewise were effective catalysts. Their activities approach that of the ammonium chloride/phosphoric acid mixture.

The mechanism of the catalysis appears to be through the generation of HCl as in the reaction:

$$NH_4Cl + H_3PO_4 \longrightarrow NH_4H_2PO_4 + HCl$$

The methylol group of the finishing agent is protonated by the HCl and loses water to yield a carbonium ion that subsequently reacts with cellulose. Repetition of the sequence through a second methylol group gives a crosslink between cellulose molecules. Mixtures of ammonium chloride and phosphoric acid and of ammonium dihydrogen phosphate and hydrogen chloride were equally effective as catalysts in the mild-cure treatments. This lends credence to the proposed mechanism.

Wrinkle resistance of fabrics treated with various concentrations (0.5 to 3 percent) of equimolar proportions of ammonium chloride and phosphoric acid as catalyst showed that 1 percent gives a finish almost equal to those from higher concentrations. A 2 percent concentration was adopted as optimum for most treatments. The strengths of samples treated with higher concentrations were about the same as the strength of those treated with 1 percent catalyst. Although higher concentrations of the catalyst theoretically produce greater amounts of hydrochloric acid, there was no corresponding decrease in fabric strength. When the catalyst mixture is used, an apparent built-in buffer effect obviates the severe strength losses that hydrochloric acid can produce.

Unlike mild-cure finishing with HCl catalyst, immediate neutralization and washing of the finished fabric is not necessary when the ammonium chloride/phosphoric acid catalyst is used. With the latter no strength loss occurred during a 12-week storage period due to omission of the afterwash as compared with about 30 percent loss in unwashed fabric that had been finished with HCl catalyst.

These results suggested that fabric treated under mild conditions with DMMC and the catalyst mixture could be postcured to develop high levels of wrinkle resistance and to introduce durable creases. Such a process was developed. A "sensitized", or partially cured, material is produced by treating fabric impregnated with a crosslinking agent and catalyst mixture at 60° to 100°C. It can be pressed and creased to shape, and then postcured in an oven at 100° to give fabric that is smooth and durably creased after laundering and tumble or line drying. The combination of time and temperature that is operative in this postcure treatment is markedly milder than that of the presently conventional postcure process.

Storage without an afterwash of fabric treated at temperatures below 100° C. with DMMC and ammonium chloride/phosphoric acid catalyst resulted in substantial increases in wrinkle resistance. The partial curing that results in the sensitizing treatment and storage does not preclude the introduction of creases in lighter weight fabrics upon steam pressing and postcuring. With heavier weight cottons, such as an 8 oz. twill, better creases were produced from fabric sensitized at 60° than at 100° C.

A hydrolysis study showed that the durability of a DMMC finish produced by mild-cure treatment with ammonium chloride/phosphoric acid catalyst was equal to that of pad-dry-cure finishing with magnesium chloride catalysis.

Dimethylol derivatives of ethyl, hydroxyethyl, methoxyethyl, n-propyl, and isobutyl carbamate worked well with the catalyst mixtures. Similarly, dimethylol dihydroxyethyleneurea (DMDHEU), a very popular DP agent, gave a good finish.

Although formaldehyde is known to require stronger catalysis than most crosslinking agents, it, too, could be used under mild-cure conditions with ammonium chloride/phosphoric acid catalyst or with mixtures of ammonium chloride and certain organic acids. Strength losses of treated cotton were greater than can be tolerated but were 60 percent higher than when hydrochloric acid catalyst was employed.

Treatment of polyester/cotton blend fabrics with formaldehyde and various catalyst mixtures also was investigated. DP ratings were outstanding after tumble drying (4 and above). With line drying after the full laundry cycle, DP ratings of treated 50/50 blend fabrics were similarly outstanding. Those of 65/35 blend fabrics were slightly lower after line drying than after tumble drying.

In summary, mixtures of ammonium chloride and phosphoric or certain organic acids can be used as versatile catalysts for durable press finishing of cotton or cotton-containing blend fabrics. They are intermediate in strength between the strong mineral acids and the commonly used Lewis acid salts. The catalyst mixtures are sufficiently strong for use under mild-cure conditions and have made possible a postcure finishing process for producing creases and DP properties.

FUNGICIDAL CHROME MINERAL DYEINGS BY AN IMPROVED ZIRCHROME PROCESS [SUMMARY]

by

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In 1966 a novel fungicidal chrome mineral dyeing process was discovered and developed for practical application to cotton textiles.[1] This practical "Zirchrome Process" required further development to eliminate certain byproduct alkali metal salts, which caused reduced tear strength values, limited chromium bath content, harsh fabric hand, and rewetting of the wax finished dyed fabrics.

A new "Sodium Free Zirchrome Process" has been developed, based on an "all ammonium" system, which results in uniform deep colored fungicidal dyeings of bright-green to grayish-green color shades with soft hand, negligible fabric-strength reductions, and excellent water-repellency values with wax finishing. Whereas, the original process required a two-solution system in formulation, the improved process uses a single bath formulation that is stable for 12 to 18 hours. The improved process increases bath contents of chromium and copper to 2.47 and 1.24 percent, respectively, and allows for a 0.5 to 2.0 percent zirconia variation.

The improved process was applied to both greige and scoured duck and printcloth, oven curing and steam-can curing techniques were used in pilot-plant runs. Some of these fabrics were wax finished, and the excellent results are demonstrated by evaluation tests. Physical test data with these fungicidally dyed greige and scoured fabrics show essentially no loss in breaking strength and Elmendorf tear strength in both warp and fill directions.

Chemical analyses show that, after washing and drying, the values compared with the theoretical add-ons of chromium, copper, and zirconia demonstrate the resistance of the dye and fungicide to hot water washing and subsequent durability in the treated fabric.

Soil burial and outdoor weatherings test data further confirm the effectiveness of the treatment on greige and scoured duck. Although weathering data cover only 6 months to date, an anticipated 3-year protection is based on evaluations with the original Zirchrome Process, where exposed samples were still serviceable with negligible microbiological degradation for this period of time.

Chemical cost data, based on bath costs and percent wet-pickup values in pilot plant runs indicate that the chemical costs of the "Sodium-Free Zirchrome Process" are less than 9 cents per pound of finished fabric. Although the present chemical costs are in a good range, some of the prices were based on purified or reagent grade chemicals, and considerably lower costs can be projected with crude or technical materials.

The improved "Sodium-Free Zirchrome Process" offers many decided advantages to the industry, one of which is the elimination of the critical drying of chromic chloride on duck in conventional chrome mineral dyeing. Zirchrome is much more resistant to weathering and offers much more durable protection to duck than conventionally dyed "pearl gray" fabrics.

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INSTRUMENTAL METHODS OF STUDYING SMOLDERING COMBUSTION

by

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(Presented by Paul A. Koenig)

ABSTRACT

Several instrumental methods of studying smoldering combustion have been investigated. One of those discussed is the ignition temperature for smoldering combustion in which a soldering gun is used as the heat source. High-temperature DTA techniques were used to investigate the effect of various glow retardants on smoldering combustion. Infrared spectra were used to further explain the flameless combustion process. Finally, a modified Oxygen Index Test was developed in an effort to obtain a quantitative measurement of resistance to smoldering combustion.

SUMMARY

Ignition studies. – In an effort to determine the relative resistance to ignition of various chemical treatments on cotton batting, a procedure has been established that involves wrapping a 4- x3- x1-inch piece of cotton batting around the tip of a soldering gun. The temperature is monitored by a thermocouple in contact with the tip and the temperature is controlled by a variable voltage transformer. The sample wrapped around the tip essentially creates a condition in which there is minimal heat loss to the environment. With a 2-minute exposure time, it was possible to determine an ignition temperature with a range of approximately ± 10° C. Table 1 shows some typical values obtained by this method. In all of tests conducted it was found that the addition of glow retardants never lowered and in some cases slightly raised the temperature necessary for self-sustained glowing combustion.

Table 1. Ignition temperatures

Sample	Average ignition temperature, ° C.
Cotton batting	396
Scoured and bleached cotton	412
2 percent polyvinyl chloride	450
4 percent polyvinyl chloride	436
6 percent polyvinyl chloride	441
2 percent ammonium bromide	401
5 percent ammonium bromide	392
7 percent ammonium bromide	404

High-temperature dynamic differential thermal analysis. – While ignition temperatures may be of some use in comparing one treatment with another, an instrumental technique known as differential thermal analysis, DTA, appears to be an even more useful method of studying changes in materials as they are heated. For purposes of this study an oxidizing atmosphere is necessary to observe smoldering combustion. Air rather than pure oxygen was chosen because (1) it produces a more controllable reaction and (2) it more closely simulates the environment of actual smoldering combustion. Figure 1 shows typical thermograms obtained when scoured and bleached cotton was heated in various atmospheres. The heating rate was 20° C./min.; the x-axis records the sample temperature, and the y-axis notes whether the change was exothermic or endothermic. It is noted that in 100 percent N_2 (inert atmosphere) an endothermic reaction corresponding to the pyrolysis of cellulose occurs at about 375°. When this same sample was heated in 100 percent air (20 percent oxygen), two exotherms occur. The first occurs at the same temperature as the pyrolysis reaction and has been identified as the oxidation of the volatile pyrolysis

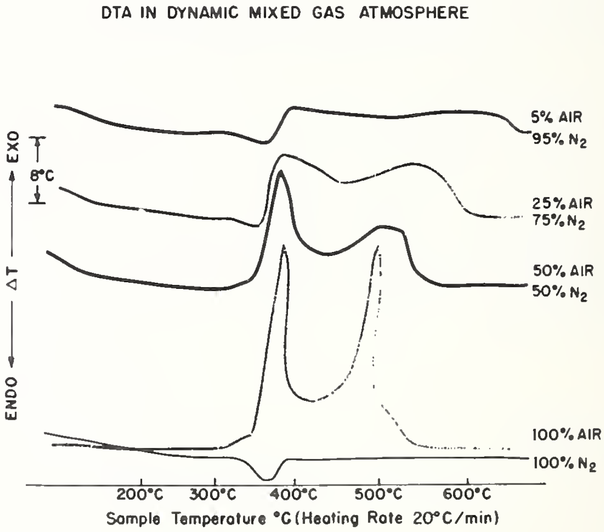

Figure 1. DTA thermograms of scoured and bleached cotton.

products. The second exotherm, which peaks at about 500° has been associated with the heat given off during the glowing combustion process. When the amount of oxygen is decreased from 10 to 1 percent, by going from 50 to 5 percent air, it can be seen that the second exotherm is more strongly affected than the first and finally at 1 percent oxygen there is a broad exothermic peak which begins at 375° C. and continues past 600° C. Figure 2 shows the effect of various concentrations of sodium borate on smoldering combustion. This Lewis base is known to be a good flame retardant but poor glow retardant. Part of this poor performance may be attributed to the fact that bases catalyze an exothermic cellulose pyrolysis reaction. It is noted that as the borax concentration is increased from 2 to 15 percent the total heat associated with the first exotherm increases. Another interesting observation is that at higher concentrations a third exothermic peak appears. The formation of sodium carbonate might be considered as a cause. At elevated temperatures there is a distinct possibility for the reaction of sodium oxide with CO_2 to form the carbonate. The heat of formation of sodium carbonate is 269.5 kcal/mole exothermic. This is 10 times greater than the heat given off during the formation of carbon monoxide and three times greater than that for carbon dioxide. Obviously, carbonate formation is undesirable.

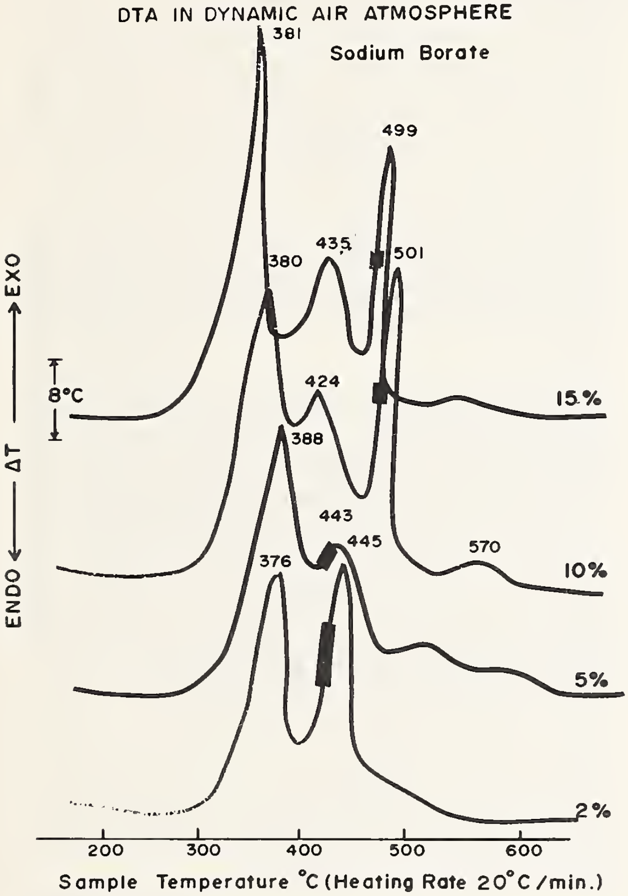

Figure 2. DTA thermograms of borax-treated cotton

Infrared studies. – In an effort to further explore possible instrumental techniques to help explain the phenomena observed during glowing combustion, infrared spectra were obtained on many of the samples discussed previously. The spectra were obtained with a Perkin-Elmer Model 137 NaCl spectrophotometer using the KBr disk technique. Figure 3 shows infrared spectra of cotton batting. This material is known to contain various impurities, including cations, which could form carbonates. The top infrared spectrum is that of unheated cotton batting and closely approximates the spectrum of scoured and bleached cotton. The samples for the 400°, 480°, and 700° C. char were prepared by heating the batting in a muffle furnace for 15 minutes and represent cotton after the occurrence of the first exotherm, second exotherm, and complete combustion, respectively. The 700° char is essentially the white ash left after complete combustion of the carbonaceous char. The infrared curve shows strong absorption at 870 cm.$^{-1}$ and 1,110 cm.$^{-1}$ as well as in the 1,400 to 1,500 cm.$^{-1}$ and 300 cm.$^{-1}$ range which is indicative of inorganic carbonates. Hence, there is evidence for carbonate formation during the smoldering combustion of cotton batting.

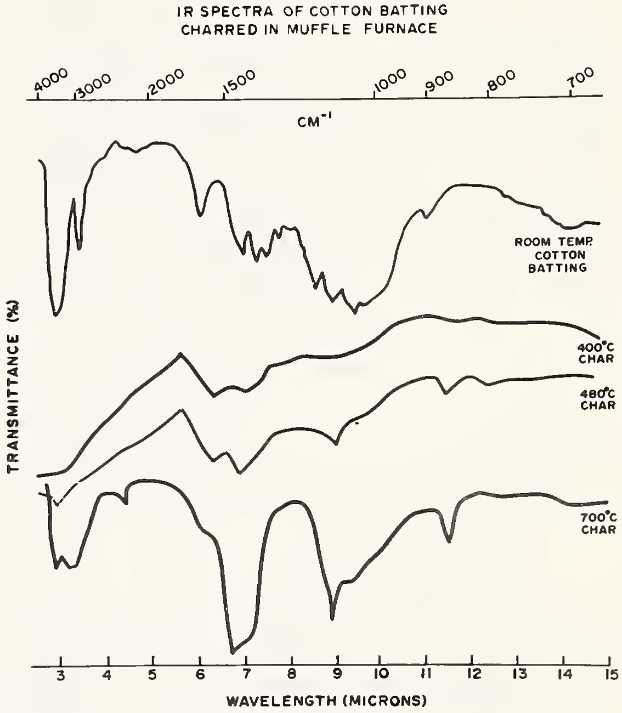

Figure 3. Infrared spectra of cotton batting

A similar infrared study was attempted on samples treated with 10 percent sodium borate. However, the spectra of the residue was essentially that of borax and since it absorbs in most of the same frequencies as the carbonates, evidence of possible carbonate formation is effectively masked.

Oxygen index studies. – One of the goals of this research is to develop a more quantitative measurement of glowing combustion. It was hoped that the oxygen index (O.I.), or "candle test," method of determining relative resistance of flaming combustion could also be used, with some modification of procedure, to obtain a quantitative measurement of resistance to smoldering combustion. The test essentially consists of the candle-like burning of a sample in the minimum amount of oxygen required to support continuing combustion. In the modified procedure the sample of material is contacted with a glowing coil until uniform smoldering combustion commences. If the sample smolders more than 3 minutes, the oxygen concentration is lowered and the test repeated until the minimum oxygen concentration is found that will support smoldering combustion for at least 3 minutes. It was found that flow rates approximately one-half the 4 cm/second used in flaming combustion were necessary to perform an oxygen index determination for smoldering combustion.

Table 2 illustrates the oxygen indexes obtained from various cotton samples. The values of 0.179 obtained for cotton batting and 0.174 for scoured and bleached cotton cloth indicate, of course, that glowing combustion is self-sustaining at oxygen concentrations below that existing in air. Table 2 also demonstrates that the addition of small amounts of synthetic fibers increases the oxygen index. This is probably due to the heat absorbing capacity of the thermoplastic materials upon melting. It can also be seen that the O.I. values increase with concentration for a series of three batting samples treated with a polyvinyl chloride emulsion.

Table 2. Oxygen index for smoldering combustion of batting

Sample	Oxygen index
Control batting	0.179
Scoured and bleached cloth	.174
5 percent nylon blend	.214
5 percent polyester blend	.192
2 percent polyvinyl chloride	.244
4 percent polyvinyl chloride	.262
6 percent polyvinyl chloride	.304
2 percent ammonium bromide	.226

Conclusions. – The work reported in this paper has, it is hoped, provided a general framework around which much more detailed investigations into the mechanisms and kinetics of smoldering combustion can be conducted. The use of ignition temperatures as a measure of resistance to smoldering combustion has indicated that certain treatments raise the temperature at which self-sustained ignition will occur, but no treatment was found that raised the ignition temperature above the 500° C. temperature which can be produced by a glowing cigarette.

The use of high temperature dynamic DTA in air appears to offer promise as a means of studying mechanisms by which various glow retardant systems function. Thermogravimetric studies should complement this work.

Infrared analysis of the residues of samples which underwent base catalyzed pyrolysis appears to indicate the possibility of carbonate formation as a reaction deleterious to the prevention of smoldering combustion. Further work is needed to confirm this observation.

Finally, the use of the oxygen index appears to be the most promising technique available to obtain a rapid quantitative measure of resistance to smoldering combustion. The effect of such parameters as sample thickness and density, gas flow-rate, and environmental temperature have yet to be fully evaluated.

SESSION IV: Joseph E. Clark, National Bureau of Standards, Washington, D.C., Chairman

OXYGEN INDEX STUDIES ON FLAME RETARDANT COTTON AND BLEND TEXTILES [SUMMARY]

by

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(Presented by James E. Hendrix)

ABSTRACT

The flammability properties of textiles fabricated from cotton cellulose and from cotton/polyester blends were investigated using the oxygen technique. Environmental temperatures during testing varied from −50° to 260° C. Moisture contents of fabric samples ranged from 0 to 40 percent.

Represented in this study are 100 percent cottons, 65/35 and 50/50 cotton/polyester blends, and 100 percent polyester. Flame retardants utilized in treating these fabrics include THPOH-NH_3, THPOH-amide, THPC-APO, THPC-cyanamide, PNE-$CHBr_3$, and a commercially applied phosphonate.

INTRODUCTION

Recently the oxygen index (OI) technique developed by Fenimore and Martin (3) has been under consideration for use as a flammability test for textiles (2, 4, 8). Work at this laboratory has shown, however, that the test is greatly affected by variables such as environmental temperature, fabric weight and construction, and moisture content of samples tested (5, 6, 7). It is necessary, therefore, that such variables be defined before the test method can be accurately evaluated as a flammability standard.

Initial investigations showed that OI values decrease with increasing environmental temperatures and that the testing environment heats up during testing. This indicates that careful control of environmental temperatures is necessary to avoid erroneous results. Additionally, the recently published test method for plastics (1) notes that moisture might affect certain OI values. Thus, this work was undertaken to more completely investigate effects of these variables (moisture content and environmental temperature) on OI values.

EXPERIMENTAL

Chimney temperatures were determined with a thermometer placed between the heat source and the glass chimney of the apparatus. Temperatures above 25° C. were attained by wrapping the chimney with a heating tape controlled with a variac. Subzero temperatures were attained by wrapping the chimney with a polypropylene bag containing dry ice. All samples were allowed to equilibrate 3 minutes before testing.

The relationship between chimney and sample temperatures is good. The sample temperatures corresponding to a chimney temperature of −60° C. is approximately −29°, while for a chimney at 250° the sample is near 205°. In the discussion of the data, reference will be made to chimney temperatures bearing in mind the existing relationship.

Moisture contents of fabrics were determined gravimetrically and calculated for the bone-dry specimen. Time required for testing was kept constant to normalize errors related to drying.

RESULTS AND DISCUSSION

Cotton fabrics having varying weights and constructions exhibit decreasing OI's over the −50° to 150° C. chimney temperature range. This decrease probably results from incremental drying of the sample during the conditioning period prior to ignition. From 150° to 180° there is little change in OI values, but above 180° OI values decrease rapidly. This decrease occurs in the same temperature range and is probably attributable to exothermic scorching which heats the sample nearer its pyrolysis temperature.

Behavior similar to that observed for untreated cotton was observed for flame retarded fabrics. These samples, however, exhibited much higher OI values at low chimney temperatures, and the OI decrease above the scorch point was of a lesser magnitude. Varying add-ons of flame retardant finish gave parallel OI vs. chimney temperature relationships.

Cotton/polyester blend fabrics (50/50 and 65/35) of comparable weights have OI values very close to those for cotton over the −50° to 265° C. chimney temperature range. Polyester, on the other hand, has temperature-dependent values, which are higher than and completely different from cotton or cotton/polyester blends.

Cotton and cotton/polyester blend fabrics treated with THPC-based flame retardants have widely separated OI values at low chimney temperatures. At high temperatures, the OI's for the different fabrics converged toward a common value (0.24).

Moisture retained by textile materials has dramatic effects on resultant OI values. Effects on cotton cellulose are minimum at moisture contents less than 6 percent; the effects become more dramatic at higher levels. Polyester is very sensitive to moisture at contents less than 1 percent. Above this level, values increase essentially linearly. Cotton/polyester blends exhibit differences in OI values dependent on the blend ratios, but respond to moisture in a manner more similar to cotton than to polyester.

The OI values for cotton fabrics treated with flame-retardant finishes are more sensitive to moisture at contents lower than 10 percent than are those for untreated cottons. This sensitivity increases with increasing add-ons of flame retardant. At high add-ons the relationship becomes very complex; this indicates that moisture might have significant effects on OI values other than those related to simple utilization of heat.

CONCLUSIONS

Environmental temperatures during testing and moisture contents of the samples have dramatic effects on OI values obtained. Thus, for OI values to retain practical value for flammability testing, these variables must be standardized and controlled.

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OXIDATION PROCESSES FOR IMPROVING THE STABILITY OF THPC-TYPE FLAME RETARDANTS
[SUMMARY]

by

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(Presented by Laurence W. Mazzeno, Jr.)

Studies of the deterioration of flame-retardant finishes have been intensified in recent years. The THPOH-NH_3 finish that has proved stable to moderate laundering and tumble drying degraded rapidly on laundering after brief exposures to sunlight. Methods of improving the UV stability of this finish are currently under investigation. Preliminary experiments have indicated that oxidation of the phosphorus is beneficial.[1] In this investigation various parameters, including time, temperature, type and concentration of reagent, have been studied in the oxidation of THPOH-NH_3-finished fabrics. Weather-Ometer exposure and laundering with line drying were utilized as UV exposure tests. Both ranked fabrics in comparable order. Vertical flame tests and changes in the phosphorus and nitrogen content after exposure have been used to determine the UV resistance of the treated fabrics.[2]

Basic fabrics used in these tests were cotton printcloth and twill that had been treated with the THPOH-NH_3 finish and given no process washing or other subsequent treatment. The standard test in the Weather-Ometer consisted of exposure to the unfiltered carbon arc for the indicated time followed by one home laundering cycle. (W.O.L. will be used in subsequent references to this procedure in this paper.)

Samples oxidized with hydrogen peroxide or sodium perborate at oxidant concentrations ranging from 0.5 to 3 percent H_2O_2 and 1 to 6 percent sodium perborate, at a temperature of 100° F. for 3 minutes, were exposed for 30, 60, 90, 150, and 210 hours. (W.O.L.). All were resistant to UV degradation through 210 hours exposure (W.O.L.). The twill fabric, with no oxidation, resisted burning after 150 hours of exposure (W.O.L.) and burned after 210 hours. Unoxidized printcloth burned after 90 hours (W.O.L.). When process washed prior to UV exposure, twill burned after 60 hours and printcloth after only 30.

Oxidation also improved the launderfastness of the THPOH-NH_3 finish. Printcloth with no oxidation failed the vertical flame test after 15 cycles of home laundering and tumble drying. All oxidized samples still showed excellent char lengths through at least 20 cycles. These laundered fabrics included samples in which the flame-retardant finishing process had been altered to utilize smaller quantities of NH_3 in the curing process. Even when the NH_3 pressure was cut to 1/8 of the standard amount, the oxidized samples did not burn after both the 15 laundering cycles and the 210 hour UV exposure (W.O.L.).

When laundered and line dried outdoors, oxidized printcloth samples showed a fourfold increase in resistance to loss in flame retardance. The increase for a comparable sateen was twofold.

Sodium hypochlorite destroyed the flame resistance of the finish. A similar oxidizing procedure, on treated twill, in which concentrations of 0.1 and 0.5 percent sodium hypochlorite were used, produced fabrics that were highly colored and burned after only 60 hours of UV exposure (W.O.L.). Daigle and coworkers have noted that home laundering in which hypochlorite bleach was used has had a deleterious effect on flame-retardant finishes.[3] They also reported that peroxide oxidation prior to the hypochlorite treatment improved the durability of the finish.

Oxidation with peroxide or perborate definitely improved the durability of the THPOH-NH_3 finish toward UV degradation. The maximum improvement possible with these reagents has not been determined. More definitive conditions for an optimum oxidation procedure are still under investigation. In the interim, because there appears to be no substantial difference between peroxide and perborate under the conditions tested thus far, it is recommended that either be used and, from an economic standpoint, the oxidation be carried out in the THPOH-NH_3 process immediately after the NH_3 cure.

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THPC-CYANAMIDE FLAME RETARDANT FINISH FOR SLEEPWEAR COTTON [SUMMARY]

by

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(Presented by Darrell J. Donaldson)

Previous work at the Southern Division has shown that THPC-cyanamide reacts in the presence of phosphoric acid to impart durable flame resistance to cotton textiles. However, the strength loss associated with this process is relatively high. It is the purpose of this paper to show that by replacement of phosphoric acid with alkali metal phosphates in the above formulation excellent flame resistance can be obtained without the excessive strength losses obtained in the earlier process.

Three sodium phosphate salts, mono–, di–, and tribasic, in concentrations ranging from 1 to 4 percent were added to a 32 percent total solids THPC (1 mole)-cyanamide (2 moles) formulation. White sateen fabric was padded with these formulations to obtain about 75 percent wet pickup, dried at 85° C., and cured at 160° for 3 to 4 minutes. The flame retardant fabrics obtained by using the dibasic sodium phosphate had better physical properties and more durable flame retardancy than those obtained by using other phosphates.

Studies were made on a pilot plant scale to determine the optimum drying and curing conditions necessary for treating fabric when the dibasic phosphate was used as the catalyst. Sateen fabric dried at 85° C. for 2 minutes and cured at 160° for 2 minutes had a 16 percent add-on and passed the standard vertical flame test after 50 laundering cycles. The treated fabric retained about 90 percent of its original breaking strength and about 30 percent of its original tearing strength. The fabric had a good hand and showed a 90° and 95° (W+F) improvement in dry and wet-wrinkle-recovery angles, respectively, as compared with untreated fabric.

This formulation was then applied to cotton flannelette. Mole ratios of from 1:1 to 1:3 THPC-cyanamide were reevaluated in the new system containing dibasic sodium phosphate. Use of a 1:2 mole ratio of THPC-cyanamide imparted the best flame resistance to fabric, with excellent durability and physical properties. Flannelette padded with a 35 percent total solids aqueous THPC-cyanamide solution containing 2.5 to 3.5 percent dibasic sodium phosphate, dried at 35° C. for 3 to 4 minutes, and cured at 160° for 3 minutes on the tenter frame passed the standard vertical flame test after 50 laundering cycles. The hand and strength of the treated fabric were good.

FLAME RESISTANT COTTON TUFTED RUGS
[SUMMARY]

by

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(Presented by John V. Beninate)

The issuance of the Standard for the Surface Flammability of Carpets and Rugs, DOC-FF1-70, by the U.S. Department of Commerce, which became effective in April 1971, has created an urgent need for effective flame retardant treatments for cotton tufted rugs.

Because of the implementation of this new standard and the recognized need for greater safety, the Southern Regional Research Laboratory is engaged in research to develop processes for applying durable phosphonium-type flame retardants to cotton tufted rugs in a commercially practical manner and which are reasonable in costs.

Three flame-retardant finishes were evaluated, (1) THPOH-amide, (2) THPC-cyanamide, and (3) THPOH-NH_3.

The THPOH-amide formulations containing THPOH, urea, and trimethylolmelamine in a molar ratio of 2:4:1 and the THPC-cyanamide in a 1:2 molar ratio were applied to tufted cotton shag rugs having sheared yarn lengths of 3/4 in. and 1 in., respectively. Solution concentrations used were 5, 8, 12, and 16 percent. The solutions were applied to the rug samples by two different methods. The first method consisted of impregnating by padding followed by brushing to raise the yarn, then drying and curing to fix the flame retardant. The second method consisted of passing the rug material through a fine spray. The amount of solution added to the fabric was just sufficient to wet the surface fibers without wetting the major portion of the base fabric. These samples were not brushed prior to the drying and curing steps, which were carried out in a forced draft oven.

The THPOH-NH_3-cured samples were treated with THPOH solution, brushed, dried, and cured in a chamber with anhydrous ammonia.

All samples treated by the techniques above were tested for surface flammability by the standard method DOC-FF1-70, commonly called the pill test. This test was conducted on the original treated samples before laundering, then on samples that were laundered 10 times by the AATCC 124-1967 (6.2III) washing and drying method. Although most treated rug samples passed the pill test before laundering, considerable differences in surface flammability were measured after the samples were laundered 10 times. In most cases, the treated rug samples with the shorter yarn length retained flame resistance after laundering better than those with longer yarn length. Phosphorus contents were obtained on treated fabrics before and after laundering to determine the degree of retention of the flame retardant polymer in the treated fibers.

The THPOH-amide flame-retardant treatment and the THPC-cyanamide treatment imparted an added property to the cotton shag rugs, which was improved resiliency. This property was measured by exposing the treated samples to a cyclic compression loading instrument, designed and developed by the Engineering and Development Laboratory of the Southern Regional Research Laboratory, which is used to measure resilience and resistence to compressional set of cotton batting. In most cases, treated samples with the higher add-ons of flame-retardant polymer had better resiliency properties; and, in general, the rugs with shorter yarn lengths had greater resiliency.

The THPOH-amide flame retardant and the THPC-cyanamide treatment were applied to yardages of short-yarn cotton walk-on mats by a pad-dry-cure method using pilot-plant equipment to determine the commercial feasibility of the process. The pilot-plant process is described.

FLAME-RETARDANT KNITS
[SUMMARY]

by

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(Presented by Jerry P. Moreau)

Processes for imparting durable flame resistance to woven cotton fabrics have been available for several years. However, such processes have not been studied for use on knit fabrics. Because of the economic advantage in making fabrics, by knitting rather than weaving, the use of knit fabrics especially in the outer wearing apparel market, is growing rapidly. With the passage of the amendment to the Flammable Fabrics Act in 1967, it is almost mandatory that techniques and finishes be developed for use in imparting durable flame resistance to knit fabrics especially since large yardages of this type fabrics go into the production of children's sleepwear.

The major disadvantages of cotton knits in many clothing end uses are their limpness, lack of dimensional stability, and inability to hold a sharp crease. The present work explores the possibility of chemical finishing of knits to impart flame resistance and to increase dimensional stability without changing the comfort factor inherent in the knit structure.

Three 100 percent cotton single knit fabrics and one double knit fabric were used in this study: a 4.7 oz./sq. yd., single-knit, plain jersey with a tight weave; a 6.2 oz./sq. yd., single knit, fancy jersey; and a 6.9 oz./sq. yd., single knit, plain jersey with an open weave. A 9.5 oz./sq. yd., double knit, swiss pique, mercerized and nonmercerized.

These knits were treated with three flame-retardant finishes developed at the Southern Regional Research Laboratory: THPOH-NH_3, THPOH-TMM-urea, and THPC-cyanamide. Pad bath concentration was varied, as well as drying and curing conditions, to develop the optimum conditions and technique for imparting durable flame resistance and maintaining the desirable properties inherent in the untreated knit fabrics.

Fabrics processed with all three finishes produced very good flame retardancy and were durable to home laundering; however, the THPC-cyanamide finish was not durable to a 3-hour soap-soda boil. At comprable add-ons, the THPOH-NH_3 treatment gave better strength retention as indicated by Mullen's Bursting Test. For the lightweight, single knit, strength retention was 94, 80, and 69 percent for THPOH-NH_3, THPOH-TMM-urea, and THPC-cyanamide treatments, respectively. For the mercerized double knit, all three treatments had $>$90 percent strength retention.

In general, the THPOH-NH_3 treatments gave the best hand, particularly with the lightweight and open-weave knits but a slightly harsher hand on the double knits as compared with the pad-dry-cure treatments.

The THPOH-NH_3 treatment appears to deposit more polymer between the fibers than does the pad-dry-cure treatments, as shown by dyed cross sections of the fibers. This may be the reason why the THPOH-TMM-urea and THPC-cyanamide treatments had less loss in air permeability than did the THPOH-NH_3 treatment.

It was shown that high levels of the crosslinking flame retardants produced fabrics with greater dimensional stability.

SESSION V: David M. Tally, Jr., Hanes Corporation, Winston-Salem, N. C., Chairman

COMMERCIAL-TYPE FABRICS FROM MEDIUM STAPLE DISCOUNT COTTON [SUMMARY]

by

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(Presented by Gain L. Louis)

Four sets of experimental fabrics were woven from a series of mixes of low–, medium–, and high-Micronaire Reading medium staple cottons in the following percentage ratio:

Lots	Micronaire Reading						Probable savings[1] ($/500 lb.)
	2.8	3.1	4.4	5.1	5.5	Average	
	Pct.	Pct.	Pct.	Pct.	Pct.		
C (Control)	–	–	100	–	–	4.4	0
1	–	10	70	20	–	4.3	1.59
2	10	–	70	–	20	4.3	2.95
3	–	20	30	50	–	4.3	3.54
4	–	30	–	70	–	4.3	5.12
5	25	–	–	75	–	4.2	6.19
6	20	–	30	–	50	4.3	6.69
7	–	35	–	–	65	4.3	8.10
8	30	–	–	–	70	4.3	9.64

The experimental fabrics included 15 printcloths, nine sheetings, nine denims, and four twills. The construction of these fabrics and mechanical processing organizations were based on specifications of cooperating mills. These fabrics were produced at SRRL and were commercially finished and evaluated for marketability by the four cooperating mills.

Fiber properties of the five component cottons were similar except for varying Micronaire Readings. The two cottons with low Micronaire Reading were somewhat less mature than the others.

This paper presents selected pertinent findings based on the printcloth, sheeting, and denim phases of this investigation.

Three carding speeds were used in the printcloth phase of the investigation to study the effect of carding rate on cotton mixes with low– and high– Micronaire Reading. One set of nine lots (lots C through 8) were carded at 25 pounds per hour; two sets of three lots (lots C, 3 and 6) were carded at 34.5 and 44 pounds per hour, respectively. Except for the difference in carding rates, all other processing variables were the same for all 15 lots. In general, lots carded at 25 pounds per hour had acceptable nep counts, while lots carded at 44 pounds per hour produced not-acceptable nep counts. Two of the three lots carded at 34.5 pounds had acceptable nep counts. Lot 8 and the six lots which carded at higher rates than 25 lbs./hr. produced yarns of not acceptable appearance grade. Fourteen of the fifteen lots had spinning end breakage rates of less than 25 per 1000 spindle hours in warp yarn (31/1, 4.25 T.M.). Eleven of the fifteen lots spun at less than 35 EDMSH for filling yarn (34/1, 3.77 T.M.).

The following table shows the experimental lots having acceptable yarn or fabric properties, or both, based on statistical evaluations. P, S and D designate printcloth, sheeting and denim, respectively. When a lot has an acceptable yarn or fabric property for printcloth, sheeting or denim, it is indicated by either P, S or D.

Properties	1	2	3	4	5	6	7	8
Yarn skein strength (CSP):								
Warp..................	PS	PSD	PSD	SD	D	–	–	–
Filling................	PSD	PD	PSD	PD	D	–	–	–
Yarn variability (%C·V·):								
Warp..................	PD	P	PD	D	D	P	P	D
Filling................	D	PD	PSD	D	D	–	–	–
Finished fabric breaking strength:								
Warp direction...	PSD	PS	PS	PS	PS	PS	P	P
Filling direction.	PSD	PS	PS	PSD	PS	PSD	PS	PSD

All the fabrics produced in this investigation were marketable without penalty as determined by mill marketing panel evaluations. Savings of about $2 to $10 per bale can be realized in mixes used for this experiment. These results were obtained by closely controlling the average Micronaire Reading of the bales, resultant mixes, and the blending and processing techniques.

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[1] Based on 12-market cotton price averages for the month of November, 1970.

COMMERCIAL TYPE FABRICS FROM SHORT STAPLE COTTON [SUMMARY]

by

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(Presented by Jack D. Towery)

In a previous project, USDA 12-14-100-9509(72), feasibility, and in some cases desirability, of blending color grades of cotton and different levels of linear density was reported at the Tenth Cotton Utilization Research Conference. Different combinations within a staple length (all in the short-staple range) were shown to perform as well as those cottons with narrow parameter limits, as represented by control cottons. The only requirement appeared to be that a high level of blending efficiency be maintained.

The present report is a continuation of the earlier work, and again is a contract project with Southern Marketing and Nutrition Research Division, USDA 12-14-100-9556(72).

One of the blend combinations of the previous project was selected in order to produce fabrics which could be used in a host of end-products. The fabrics chosen were selected to fit the capability of the Textile Research Center. For example, a corduroy could have been made rather than a bedford cord. There was no limit to the types of fabrics that could have been chosen. Nine fabrics – three representing industrial fabrics, three apparel, and three representing household usage – were selected.

Twenty-eight bales were processed in a three-color, two linear-density (micronaire) blend. Rather wide variations were chosen, all of which could be considered to be "discount" cottons. Strict Low Middling White cotton with an average micronaire of 5.6 was approximately 58 percent of the blend. Low Middling Light Spot grade with a 2.9 micronaire was the second blend component and accounted for 21 percent of the cotton used. The third component was a Low Middling Spot grade with an average micronaire of 2.7. All were purchased as 1-inch staple and average 84,000 p.s.i. (41.7 g./tex). Average loan value in the market of this blend was 15.16 cents per pound as compared with a Strict Low Middling White cotton of 18.50 cents per pound, 20.20 basis. When a correction for the higher nonlint level is used (for the lower grades), there is a savings of $15.00 per bale in raw material cost.

The rather odd blending percentages were required to achieve a 4.0 micronaire. Finisher drawing sliver averaged 3.98 with a 1.68 percent coefficient of variation, indicating not only a successful micronaire but a high level of blending efficiency. Blending followed the same procedures as those that would be used on a three-component, synthetic-cotton mixture. Mill-scale weigh-pan hoppers metered the blend in a continuous sandwich. Laps were mixed on the cards to eliminate the time component in blending conditions. Further blending was achieved by alternating card slivers from the two cards behind the drawing.

Neps averaged 6.7 per 100 sq. inches. Finisher drawing sliver uniformity averaged 4.1 percent. Ends down per 1,000 spindle hours were 10 for 15/1, 14 for 16/1, and 16 for 17/1, with spindle speeds ranging from 11,000 r.p.m. for the 24/1 warp to 5,000 r.p.m. for the 6.8/1 filling. Yarn strength ranged from a breakfactor of 2,000 to 2,200.

The fabric quality was equal to or better than commercial fabrics. The fabrics produced were:

Apparel types:

1. 3/2 R.H. twill, piece-dyed denim
   48" 86 x 48 – 1.65
   14/1 warp and 14/1 filling
2. Bedford cord
   48" 26 x 50 – 2.00
   14/1 warp and 14/1 filling
3. 2/1 L.H. twill, pocket drill
   37" 72 x 44 – 2.40
   14/1 warp and 14/1 filling

Household types:

4. Bark cloth
   36" 88 x 38 – 2.30
   14/1 warp and 14/1 filling
5. Huck toweling
   18" 84 x 42 – 5.20
   17/1 warp and 15/1 filling
6. Terry toweling
   26" 64 x 40 – 1.80
   24/2 ground warp, 15/1 pile warp, and 12/1 filling

Industrial types:

7. Shoe duck
   37" 50 x 36 – 2.00
   13/2 warp and 18/2 filling
8. 2/2 twill, Canton flannel
   37" 64 x 44 – 2.00

17.1 warp and 6.8/1 filling

9. Industrial sheeting
   39" 48 x 48 – 2.85
   14/1 warp and 14/1 filling

The griege phase of this project has been completed. The finishing phase is currently underway.

In finishing, the bedford cord and the piece-dyed denim are to receive the same procedural treatment. Both will be brushed, singed, desized, caustic steamed, bleached, dyed, and have a durable press treatment applied. The bark cloth will be desized, caustic steamed, bleached, dyed, "hand" modified, latex backed, and have a soil/oil repellent treatment. The terry toweling will receive a desizing and caustic steaming, followed by bleaching and dyeing, and then have a softening agent applied. The huck toweling will be carried through bleaching only. The Canton flannel has been napped, and the pocket drill has been Sanforized. The shoe duck and sheeting do not receive further treatment.

The Canton flannel was napped in one mill, and the pocket drill was Sanforized in a second plant. Both fabrics attracted attention with their cleanliness and smoothness. Mill personnel expressed surprise that this blend of cotton would produce high-quality fabrics.

Preliminary tests have indicated no dyeing skitteriness will be encountered.

PROPERTIES OF DURABLE PRESS FABRICS PRODUCED FROM BLENDS OF RESIN TREATED AND UNTREATED COTTON FIBERS

by

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INTRODUCTION

The work to be described forms part of an extended study of the characteristics of fabrics made from a 50/50 blend of resin treated and untreated cotton fibers. In an earlier part of the work which was described a year ago, the influence of a number of construction variables was examined. The results of this study indicated that those factors that improved the dimensional stability of the fabrics often had an adverse effect on their abrasion resistance. In the three weaves that were used (plain weaves, 3/1 twills, 3/2 twills), the plain weaves had the best dimensional stability but showed the poorest abrasion resistance. Singles filling yarns gave lower shrinkage but poorer resistance to abrasion than plied filling yarns. Fabrics that were woven tightly shrank less but abraded more than those that were more open.

The next phase of the work, described herein, was designed to attempt to produce fabrics having both good dimensional stability and good abrasion resistance either by using a construction based on the best compromise that could be developed from the results of the first phase of the work or by attempting to improve either the dimensional stability or the abrasion resistance, or both, of an inadequate construction through the use of mechanical finishing techniques.

Fabric design. – The constructions that were selected are outlined in table 1. All three weaves are represented, though the 3/2 twills are emphasized because of their superior all around performance in phase I. Four of the twelve fabrics that were made were intended to be used without additional treatment (numbers 115, 118, 121, and 124). These were designed to have a reasonably high cover factor to obtain optimum dimensional stability. The remaining eight fabrics were designed with low filling cover factors to provide for mechanical shrinkage in finishing. In order to make for easier processing the yarns that were used were coarser and had higher twist multipliers than those used in the first phase, even though the use of such yarns would be expected to result in a somewhat reduced dimensional stability and a poorer abrasion resistance.

Table 1. Fabric constructions

Fabric number	Weave	Weight (oz./sq. yd.)	Ends x picks per inch
Nominal 6.0 oz. sq. yd. fabrics:			
115	Plain	5.6	74x52
116	3/1	5.7	74x58
117	3/1	5.2	74x74
118	3/2	6.1	73x66
119	3/2	5.3	74x74
120	3/2	6.4	72x61
Nominal 8.0 oz./sq. yd. fabrics:			
121	Plain	6.7	65x44
122	3/1	7.0	63x56
123	3/1	7.7	65x75
124	3/2	7.4	67x68
125	3/2	7.9	67x78
126	3/2	8.7	63x46

Fiber resin treatment. – Resin treatment of the fiber was carried out in stock dyeing equipment consisting of a dye kier equipped with an air extracting system and a stock dryer. Formulations were adjusted to give an add-on of 10 to 12 percent Permafresh 183 resin. After air extraction, drying to a moisture content of about 20 percent was carried out in a stock dryer operating at a temperature of 190° to 200° F. This relatively low drying temperature was used to minimize the likelihood that any appreciable amount of curing would occur.

Blending with an equal weight of untreated fiber was done at the picker. In general, the blending and picking, as well as carding to drawing operations and the roving operation, were accomplished satisfactorily. Throughout the processing, however, it was noted that the fiber fly and waste was predominantly blue, the color that had been used to identify the resin treated component of the fiber blend. Yarns spinning presented some difficulty. Spindle speeds had to be reduced and even then the ends down were about 100 per thousand spindle hours for the heavy yarns and 160 per thousand spindle hours for the lighter yarns.

Warp preparation was accomplished satisfactorily in spite of the fact that no size was applied in order to prevent possible migration of the resin to the untreated fiber. This lack of warp size made the weaving somewhat difficult because of excessive fly and a higher number of warp breaks than would be normal for a properly sized cotton yarn. In spite of the difficulties, however, acceptable fabrics were made.

Finishing treatments. – As already mentioned, the two plain woven fabrics and two of the 3/2 twills were designed to be used without any subsequent mechanical finishing. These designs were based on the findings of the first phase of the work as well as a desire to produce fabrics weighing approximately 6 or 8 oz./sq. yd.

The mechanical finishing treatments that were used were designed to preshrink the fabrics in a variety of ways in order to reduce the tendency of the fabrics to shrink in subsequent laundering. In addition, the treatments altered the distribution and magnitude of yarn crimp within the structure, which could have a beneficial effect on some of the other characteristics such as abrasion resistance. Two fabric constructions were selected from each weight class for each of the mechanical finishing treatments, as follows:

1. *FRL® compactor.* – Length reduction of approximately 5 and 15 percent was used, with back tensions of 0.5 and 1 lb./in. of width for fabrics 116, 119, 123, and 125. Also, approximately 10 percent length reduction was used at a back tension of 4 lb./in. of width. The use of back tension was intended to reduce the width of the fabric as it was entering the compactor.
2. *Sanforizer.* – Length reductions of approximately 5 and 10 percent were used with back tensions of 0.5 and 1 lb./in. of width, for fabrics 117, 120, 122, and 126.
3. *Controlled shrinkage.* – A controlled amount of warp and filling shrinkage was induced by pinning fabrics 117, 120, 122, and 126 on frames and exposing them either to 90 to 100 percent RH at 70° F. or to 100 percent RH and 200°. The filling shrinkage levels were 0 and 2 percent both at a warp shrinkage of 3 percent.
4. *Microstretch.* – The Cluett Peabody Microstretch unit was used to reduce 5 percent filling stretch in fabrics 116, 119, 123, and 125 under 0 warp restraint. In this way, filling crimp was decreased and warp crimp was increased.
5. *Tenter frame.* – Similar crimp interchange was effected by holding the fabric in a clip tenter under 0 warp restraint and stretching the filling either 3 or 5 percent. Fabrics 116, 119, 123, and 126 were held for 16 hours under these conditions in an atmosphere of approximately 70° F. and 65 percent RH.

This resulted in a total of 64 fabric-finish combinations to be evaluated.

Evaluation. – Initial evaluation of the performance of these fabrics was done by making up pant cuffs and subjecting them to repeated washing and tumble drying cycles as has been described in several USDA publications. Cuff specimens were prepared by cutting two fabric samples from the same fabric location 18 by 11 inches with the long dimension in the warp direction. The fabrics were then overlapped 3/4 inch and stitched lengthwise with a lockstitch to form a tube. Cuffs were then prepared by standard procedures having a 1-7/8 inches cuff depth. The opposite end of the cuff was turned down 3/8 inch and stitched to prevent ravelling. The final test cuff specimen measured approximately 12 inches in length by 9-1/2 inches crease to crease depending, of course, upon fabric thickness and stiffness.

All of the cuff specimens were pressed on a Prosperity pants press Model MO equipped with an automatic timer to control the various functions during the press cycle. They were then cured in a horizontal-airflow oven operated at a curing temperature of 320° F. The cuffs were hung in the oven for 8 minutes, part of this time being required for the oven to recover its temperature after the door had been opened and closed.

Laundering was done in a Kenmore Model 600 automatic washer and tumble drying in a Kenmore Model 600 electric dryer. A normal wash cycle was used at a warm water temperature setting and 25 grams of Tide detergent was added to each 4 pound load.

All the cuffs were examined after 1, 10, 20, 40, and 80 launderings. At each of these steps shrinkage in both directions was measured and appearance or crease retention was evaluated on a 0 to 5 scale. The effects of abrasion were noted by counting the number of holes as they developed, as well as by quantifying the abrasion damage in a method described by E. C. Kingsbery.[1] In this technique each abrasion rating represents the sum of the number of holes falling within a specified size classification multiplied by the factor as indicated in the following table:

Hole size	Factor
1/32 in.	0.3
1/16 in.	.6
1/8 in.	1.2
1/4 in.	2.5
3/8 in.	3.8

RESULTS

The results are summarized in table 2. The useful wear life of a garment is usually terminated when holes develop. All of these fabrics have holes after 80 washings. Many of them, however, did not show any sign of abrasive damage after 40 washings. Table 2, therefore, includes the ratings after both 40 and 80 washings in order to permit evaluation of the relative merits of the treatment-fabric combinations within the useful life of the garment, as well as considerably beyond the end of what would be its normally acceptable wear life.

Shrinkage. – A garment is usually considered satisfactory if its dimensions change no more than 2 percent (based on the cured dimension) in any direction during its useful life. None of the unfinished fabrics meets this requirement, though two show warp and

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[1] Kingsbery, E. C. Private communication. January 30, 1968.

Table 2. Launderability of finished fabrics

		Number of fabrics after 40 or 80 wash-dry cycles											
		No. treatment		Compacted		Sanforized		Preshrunk		Microstretch		Tenter	
Characteristic	value	40	80	40	80	40	80	40	80	40	80	40	80
Total number in study		4		20		16		16		4		8	
Shrinkage:													
Warp	<+2 percent[1]	0	0	11	11	0	0	0	0	0	0	0	0
	> 2 percent	1	0	9	9	13	11	7	4	2	1	2	1
	2-3 percent	2	1	0	0	2	4	5	5	2	3	6	5
	> 3 percent	1	3	0	0	1	1	4	7	0	0	0	2
Filling	< 2 percent	0	0	12	11	14	9	11	4	2	2	3	2
	2-3 percent	2	1	8	6	2	7	5	10	2	1	3	4
	> 3 percent	2	3	0	3	0	0	0	2	0	1	2	2
Abrasion rating	0	2	0	15	0	12	0	9	0	3	0	4	0
	0-10	2	0	5	3	4	6	7	5	1	2	4	2
	10-20	0	2	0	15	0	10	0	11	0	2	0	3
	20	0	2	0	2	0	0	0	0	0	0	0	3
Appearance rating	> 4	4	3	20	17	16	16	16	15	4	3	8	7
	3-4	0	1	0	3	0	0	0	1	0	1	0	1
Crease retention	> 4	0	0	1	0	0	0	0	0	0	0	0	0
	3-4	3	0	15	0	5	0	5	0	3	0	7	0
	2-3	1	0	4	6	6	1	6	6	1	1	1	5
	< 2	0	4	0	14	5	15	5	10	0	3	0	3

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[1] Increase in measurement.

filling shrinkages of less than 3 percent after 40 launderings. One of these still has a shrinkage of less than 3 percent in each direction after 80 launderings. Twelve of the compacted fabrics show satisfactory dimensional control in both directions after 40 launderings and 11 of these after 80 launderings. All 20 compacted fabrics show less than a 2 percent change in the warp direction even after 80 launderings. Thirteen of the sanforized fabrics are satisfactory after 40 launderings and nine remain satisfactory after 80 launderings. Seven of the sixteen preshrunk fabrics are satisfactory after 40 launderings, and four remain satisfactory after 80 launderings. Two of the four microstretched fabrics are satisfactory after 40 launderings, and one remains satisfactory after 80 launderings. Two of the eight tentered fabrics are satisfactory after 40 launderings, and one remains satisfactory after 80 launderings.

Abrasion. – Two of the four untreated fabrics show no abrasion damage after 40 launderings. This is also true of 15 of the 20 compacted fabrics, 12 of the 16 sanforized fabrics, nine of the 16 pre-shrunk fabrics, three of the four microstretched fabrics, and four of the eight tentered fabrics.

Appearance. – All the fabrics retained a very good appearance after 40 launderings. Most of them still retained a good appearance after 80 launderings.

Crease retention. – The crease retention of these fabrics was quite disappointing. Fair crease retention after 40 launderings was exhibited by three of the four untreated fabrics, 15 of 20 compacted fabrics, five of the 16 sanforized fabrics, five of the 16 pre-shrunk fabrics, three of the four microstretched fabrics, and seven of the eight tentered fabrics. After 80 launderings, all the fabrics showed rather poor crease retention.

SUMMARY

The work carried out to date has indicated that it is possible to obtain excellent dimensional stability in fabrics made from a blend of 50 percent unresinated cotton fiber provided a suitable mechanical finishing procedure is used. The mechanical finishing methods used also imparted excellent abrasion resistance to most of the fabrics. Many of them showed no sign of abrasion damage after 40 wash-tumble dry cycles. All the fabrics examined also retained a very satisfactory flat appearance through 40 washes and many of them still were satisfactory after 80 washes. The ability of the fabrics to retain a crease, however, was disappointing. Crease retention was at best fair for a slightly over half the fabrics after 40 washings and poor for all the fabrics after 80 washings.

This work is still proceeding. Other characteristics of some of the mechanically finished fabrics are being measured, such as yarn crimp, breaking strength and elongation, tearing strength, bursting strength, flex and flat abrasion resistance, and wrinkle recovery under a variety of conditions. On the basis of these measurements, as well as those reported herein, some of the fabrics will be selected for a study of the possibility of finding a finishing treatment that will alleviate some of the deficiencies that have shown up in the laundering trials. Such finishes may, for example, improve the abrasion resistance or perhaps the crease retention.

IMPARTING MAGNETIC SUSCEPTIBILITY TO COTTON FIBERS
[SUMMARY]

by

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and

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(Presented by Devron P. Thibodeaux)

Techniques were developed for imparting paramagnetic and ferromagnetic properties to cotton fibers so that they may be manipulated by magnetostatic force fields. Magnetic susceptibilities of the treated fibers were measured by the standard Faraday technique employing an electro-microbalance and a 4-inch laboratory electro-magnet. The basic principle underlying not only the Faraday technique but also the entire concept of using magnetic fields for fiber conveyance is that magnetic materials will be translated into nonuniform magnetic fields of increasing flux density. For this reason all the evaluations of the various magnetic treatments were performed by measuring the apparent change of weight of samples suspended from the microbalance into a nonuniform magnetic field with a maximum value of magnetic energy gradient of 4.88 (kilogauss)^2/cm.

Some of the most promising of the magnetic treatment techniques that have been developed for cotton fibers are:

Paramagnetic salts. – The phenomenon of paramagnetism can only exist when atoms of a material contain partially filled electonic shells. Paramagnetic compounds are essentially those with transition group elements. The rare earth group (incomplete 4f shell) has the highest values of paramagnetic susceptibilities and the iron group (incomplete 3d shell) has the next largest values. Magnetic treatment of cotton fibers was accomplished by soaking the fibers in aqueous solutions of rare earth chlorides and sulfates and in cobalt (II) and iron (III) chlorides. The magnetic force to sample weight ratio (F_m/W) was measured for several different techniques using both Memphis rain-grown and Acala irrigated cotton. These cottons were treated as raw cotton fibers and as premercerized fibers. Selected results for treatments using some of the rare earth chlorides are shown in table 1. Data is included on the add-on of paramagnetic salts and the resulting magnetic force to sample weight ratio for the maximum magnetic field gradient.

Table 1. Paramagnetic properties of cotton treated with rare earth salts

	Raw cotton		Mercerized cotton	
Compound	Mass fraction of paramagnetic salt	F_m/W	Mass fraction of paramagnetic salt	F_m/W
		Rain-grown cotton		
$DyCl_3.6H_2O$	0.515	0.208	0.700	0.289
$TbCl_3.6H_2O$	.653	.253	.729	.257
$HoCl_3.6H_2O$	.543	.189	.639	.241
$GdCl_3.6H_2O$	.579	.128	.694	.179
		Irrigated cotton		
$DyCl_3.6H_2O$	.681	.302	.679	.315
$TbCl_3.6H_2O$	.456	.199	.622	.238
$HoCl_3.6H_2O$	.531	.231	.512	.251
$GdCl_3.6H_2O$	.419	.159	.630	.192

Slightly higher F_m/W values are obtained when treating the irrigated cotton as compared with the rain-grown cotton. Mercerizing the cotton prior to treatment with the aqueous rare earth salt solution enhances the F_m/W ratio.

Organometallics. – It was postulated that treating cotton with metal-organic compounds might allow for the cellulose molecules to be attached to transition metal atoms through the organic ligand. Two classes of organometallics were tried, including the cyclopentadienyls of iron [$(C_5H_5)Fe$] and nickel [$(C_5H_5)Ni$] and the acetylacetonates of dysprosium [$CH_3COCHCOCH_3)_3Dy$] and holmium [$(CH_3COCHCOCH_3)_3Ho$]. Solutions of these organometallics were prepared with hydrocarbon solvents and were applied to cotton fibers. The cyclopentadienyls (metallocenes) showed minimal magnetic susceptibility, due probably to the organics chelating to the unpaired electrons in the 3d shells of the iron and nickel. Treatment of both types of cotton with the rare earth acetylacetonates gave much better results. These data are shown in table 2. Values of F_m/W are comparable to data obtained with the rare earth chlorides (table 1). This is probably the result of the effective shielding of the inner unfilled 4f shells of the rare earth atoms from organic chelating bonds.

Ferromagnetic micro-particles. – Magnetic susceptibilities of ferromagnetic materials are at least three orders of magnitude greater than those for paramagnetic materials. Unfortunately, ferromagnetism is a property of bulk crystalline matter, which is required for the necessary interatomic exchange forces. This necessitates that solid-state ferromagnetic elements or alloys be deposited onto the cotton. The most feasible approach is to attach to the cotton, ferromagnetic microparticles whose diameters are small compared with the cotton fiber diameters. Table 3 lists the composition and magnetic properties of the most promising ferromagnetic particles that could be used. Only 1 or 2 percent by weight of these ferromagnetic materials added to cotton fibers should result in F_m/W ratios of between one and seven for low magnetic fields.

Several techniques were examined for uniformly attaching ferro-powders to cotton fibers: suspensions of

Table 2. Magnetic susceptibilities of irrigated and rain-grown cotton fibers treated with rare earth organometallics

	Compound	Organometallic mass fraction	F_m/W
Rain-grown cotton	$(CH_3COCHCOCH_3)_3Dy$	0.65	0.270
	$(CH_3COCHCOCH_3)_3Ho$	.255	.158
Irrigated cotton	$(CH_3COCHCOCH_3)_3Dy$	.614	.239
	$(CH_3COCHCOCH_3)_3Ho$	.479	.251

Table 3. Composition and magnetic properties of various candidate ferromagnetic particles

Ferromagnetic powder	Average particle size (microns)	Minimum composition	F_m/W @4.88 KG^2/cm
Carbonyl iron type E	4-6	98.0 percent Fe	312.0
Carbonyl iron type SF	3-4	98.0 percent Fe	281.6
Carbonyl iron type W	2-4	92.5 percent Fe	195.1
Carbonyl iron type L	3-9	99.5 percent Fe	368.4
Ultra-pure nickel	<20	99.0 percent Ni	79.9

catalytic nickel powders dispersed in a paraffin wax-hexane solution, finely divided carbonyl iron particles dispersed in a solution of polyethylene oxide polymer, and carbonyl iron particles dispersed in solutions of partially neutralized oleic acid surfactant. The most effective treatment technique was the dispersed carbonyl iron particles sprayed onto the fibers, allowing the particles to wet the surface and to attach nonrigidly. These agents lubricate the fibers and allow mechanical manipulation to uniformly distribute the particles along the length of the fibers. Magnetic measurements on treated single fibers and fiber tufts show that uniform values of F_m/W between three and five are practical.

Preliminary experimentation has been carried out on the "electroless" plating of ferromagnetic nickel particles onto cotton fibers. The very fine particles deposited onto the fiber surface appear to be permanently attached and give magnetic force to weight ratios between 0.5 and 0.7.

This research has shown that it is possible to impart magnetic susceptibility to cotton fibers. The techniques developed can be applicable at commercial processing levels. Preliminary tests show that most of the treatments are removable, that the specific compounds are recoverable, and that the physical properties of the treated fibers are essentially unaltered.

INFLUENCE OF TEMPERATURE AND HUMIDITY ON THE FORCES FOR SEPARATING COTTON FIBERS

[SUMMARY]

by

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INTRODUCTION

The Southern Division's research toward developing a fundamentally new system for processing cotton into textiles has been primarily concerned with the study of aerodynamics, electrostatics, and ultrasonics for manipulating cotton fibers. The research has shown that individualizing fibers is the most important requirement and the most difficult obstacle to the development of a new system. A study, therefore, has been conducted to determine if there exists a specific combination of temperature and humidity conditions under which cotton fibers possess a greater tendency to separate one from another.

EXPERIMENTAL

It was postulated that measurement of the change of drafting forces of card silver closely approximated opening force conditions and could be correlated with the forces required to separate fibers; such measurements were made on a West Point Cohesion Tester.

The Cohesion Tester was mounted within an environmental chamber, to allow the measurements to be made at preselected temperatures and humidity conditions. The chamber was provided with "work through" gloves and an analytic balance mounted on top of the chamber with the weighing arm fed through to the inside of the chamber.

The signal output from the Cohesion Tester was fed through a carrier preamplifier into a two channel electronic recorder equipped with an integrator.

A mill-type cotton blend was processed into picker laps and carded into 55-grain sliver for use in all tests.

To measure the influence of temperature and humidity on the forces to separate cotton fiber, individual tests were statistically designed so that the interaction of all contributing parameters could be determined. Selection of temperature and humidity combinations were made to statistically cover the designed output of the environmental chamber. The order of testing for different humidities at a given temperature was randomized.

Five determinations and two replications were made at each combination of temperature and humidity. The assignment of sliver containing different portions of the picker lap to the various combinations of temperature and humidity tested was randomized in order to equalize the effects of lap locations on these combinations.

Enough sliver to perform five determinations at a given temperature and humidity setting was placed in the environmental chamber and allowed to come to equilibrium with the preselected atmospheric conditions. Data was recorded for a sample running for 4 minutes. The recorded data was reduced to absolute drafting force by mechanical integration of the recorded wave.

RESULTS AND DISCUSSION

It was shown from a statistical analysis of the recorded data that there was a consistent and highly significant decrease in average drafting force or the force required to separate fibers, with increases in temperature (fig. 1) and relative humidity (fig. 2). The overall decrease in average drafting forces with increases in temperature at various relative humidities is linear.

Further statistical analysis showed a tendency for the decrease in average drafting force to level off slightly at the 121° and 138° F. values. The decrease in average drafting force with increase in relative humidity tended to level off between the 65–, 80– and 95– percent levels for 87° and 104°, and differences in means at these levels were generally insignificant.

Figure 3 shows the variation in absolute drafting force with time at temperatures of 36°, 70°, and 138° F. keeping humidity constant. The reduction of amplitude and wavelength of drafting force wave and absolute drafting force is more pronounced with variations in temperature than with variations in humidity.

CONCLUSIONS

Results demonstrate that optimum atmospheric conditions exist for the separation of fibers with minimum force requirements. A consistent and highly significant decrease in absolute drafting force resulted with increased temperature and relative humidity. The overall decrease in absolute drafting force with increase in temperature at various humidities is linear, with a tendency for the decrease to level off at higher temperatures. No significant differences were found between absolute drafting forces at the higher levels of humidity at any temperature. The overall decrease in absolute drafting force with increase in relative humidity tends to level off rapidly for the higher humidities at the 87° and 104° F. temperature levels.

The reduction in absolute drafting force when atmospheric conditions are controlled indicates that cotton fibers can be separated with lower force requirements. The reduction in the amplitude and wavelength of the drafting force wave when atmospheric conditions are controlled facilitates more uniform fiber separation.

It can also be concluded that operating fiber separating equipment at any combination of temperature between 120 and 138° F. and humidity between 65 and 95 percent will result in a 35 to 45 percent reduction in the separation force when compared with opening-room operating conditions of about 75° to 80° F. and 50 to 55 percent relative humidity.

Application of these results for separating and individualizing fibers will be used in the development of the initial state of the new textile processing system. It is anticipated that these findings will greatly enhance fiber separation and processing efficiency.

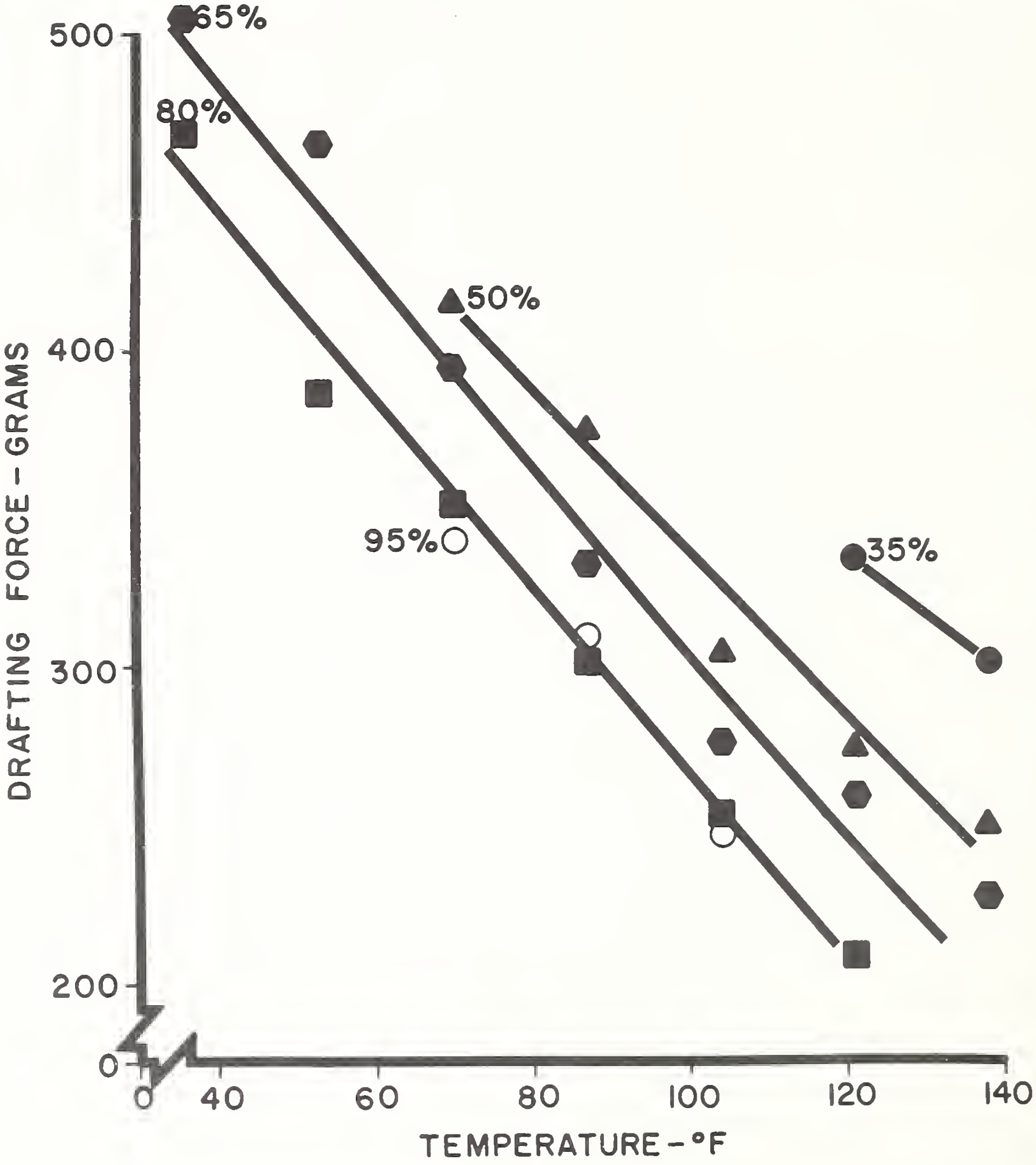

Figure 1. Effect of temperature upon the drafting force at various humidities

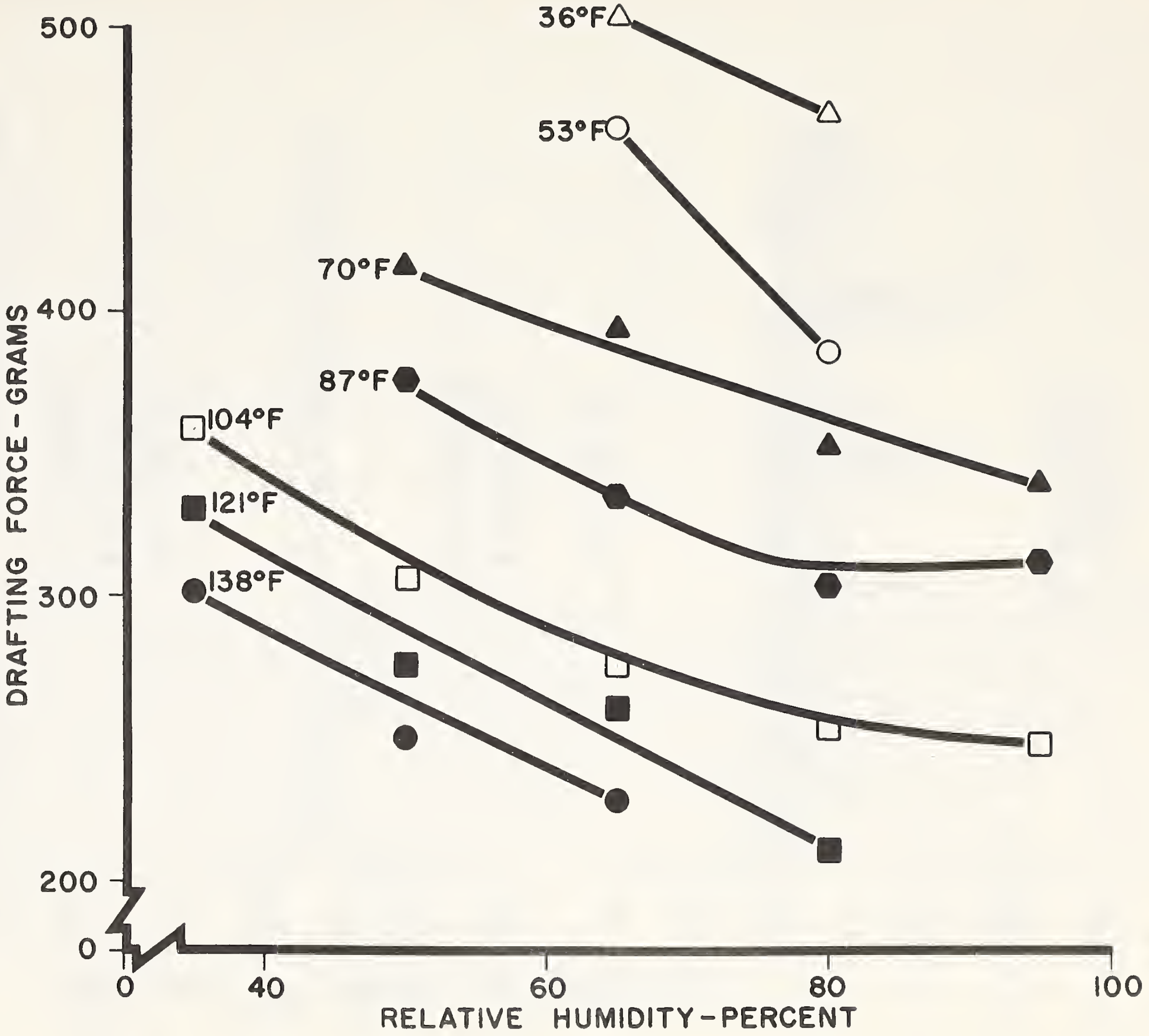

Figure 2. Effect of humidity upon the drafting force at various temperatures

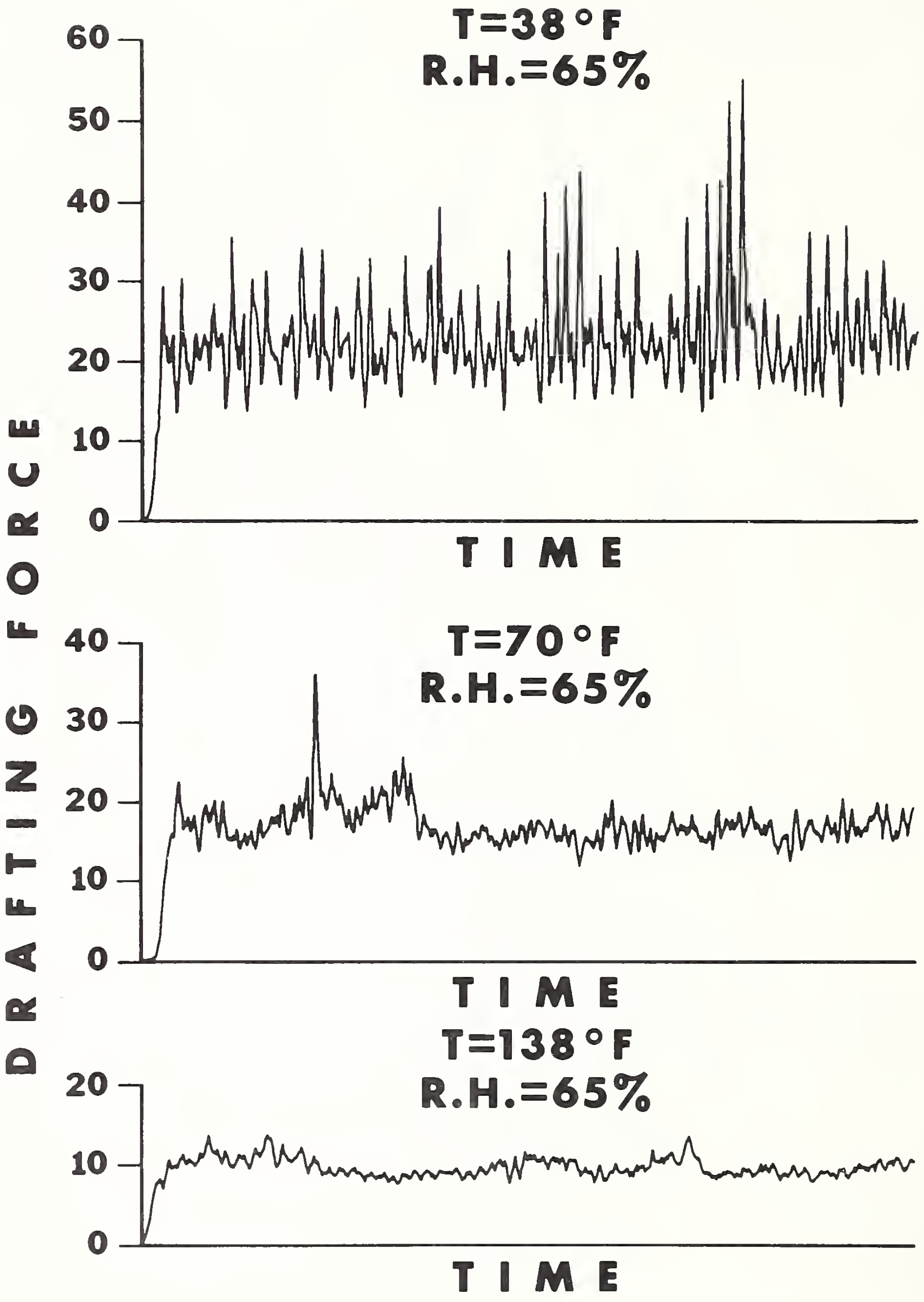

Figure 3. Drafting force traces at various temperatures for a humidity of 65 percent

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